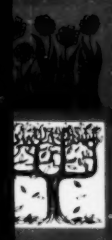

Isotopes & Radiation Technology

1971 Quarterly Technical Progress Review Volume 9-1

Prepared for Division of Technical Information – Division of Isotopes Development U.S. Atomic Energy Commission by Isotopes Information Center Oak Ridge National Laboratory

Isotopes and Radiation Technology

is a Technical Progress Review prepared by the Isotopes Information Center, Oak Ridge National Laboratory, at the request of the Divisions of Technical Information and Isotopes Development, U. S. Atomic Energy Commission. This Review is intended to assist those interested in keeping abreast of significant developments in the fields of isotopes and radiation technology. It is not a comprehensive review of all literature published in this field during a given quarter; rather, it is a mechanism for presenting concise, selected reviews of information on subjects of prevailing Commission interest as it becomes available.

This Review attempts to relate the published results of research and development sponsored by the Division of Isotopes Development to significant developments in radioisotopes and radiation technology, as reported in the world literature. Coverage includes isotope production and development, isotope technology development, isotope applications technology, process radiation development, and radiation processing of food and medical supplies.

In addition to reviews of current literature and special review articles dealing with specific isotopes, facilities, and applications, this publication occasionally contains feature articles prepared by recognized experts on specific topics of current interest. Critical evaluations and interpretations presented are those of the editors and invited reviewers; therefore readers are encouraged to consult the original references in order to obtain all the background of the work reported and the interpretation of the results given by the original authors.

Insofar as feasible all references are checked by the editors, using the library facilities of Oak Ridge National Laboratory, Oak Ridge Associated Universities, and the University of Tennessee. Occasionally, however, the cited material is not available; such cases are identified by an asterisk (*).

The subject headings listed below have been adopted to help maintain continuity and order, from one issue to the next, in the material reviewed. All reviews, except Feature Articles, will be arranged under these headings; but any one issue will not necessarily contain all the headings.

Isotope Production and Development
Isotope Technology Development
Food Irradiation
Process Radiation Development
Source Development
Isotopic Heat and Power Development
Applications in Life Sciences
Safety
Isotopes Around the World
Miscellaneous

P. S. Baker, R. H. Lafferty, Jr., Martha Gerrard, R. E. Greene,
F. E. McKinney, and Helen P. Raaen, *Editors*
A. F. Rupp, *Adviser*

OAK RIDGE NATIONAL LABORATORY

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Isotopes and Radiation Technology

Vol. 9, No. 1 Fall 1971

Contents

I Isotope Production and Development

1 **Recovery of ^{147}Pm from Savannah River Plant Waste** *Summarized by R. E. Greene*

1 Process Description
3 Plant-Test Results

II Isotope Technology Development

5 **Report on the Brussels International Conference: Radiation and Isotope Techniques in Civil Engineering, October 28–30, 1970** *George J. Rotariu and Meyer Steinberg*

5 Background
6 Highlights and Impressions
8 Availability of Information

8 **Radioisotopes in Blast-Furnace Ironmaking Operations** *W. R. Pavlik*

8 The Blast Furnace
9 The Ironmaking Process
9 Radioisotopic Analysis of Raw Materials
12 Radioisotope Applications to Raw-Materials Handling
13 Radioisotopes in Blast-Furnace-Process Gaging
14 Radioisotopes in Blast-Furnace-Process Studies
16 Radioisotope Applications to Product Analysis
17 Miscellaneous Blast-Furnace Applications
19 Conclusion

21 **Highway Applications of Nuclear Techniques** *Summarized by P. S. Baker*

23 **Neutron Activation and On-Stream Analysis in the Mineral Industries Using SHERLOCK III** *K. V. Godfrey and W. E. Downs*

24 Description of SHERLOCK III
25 Principle of Operation
26 Mill-Circuit Considerations
26 Radiation Variables for an On-Stream NAA Circuit
27 Results
30 Advantages and Disadvantages of the NAA System

31 **Recent DID Radiometric-Technique Developments** *Martha Gerrard*

31 Nuclear Helicopter Lift Indicator
32 Isotopic Shock-Wave-Position Sensor
36 Discharge Measurements Using Radioisotopes in High-Head Turbines and Pumps. II
37 Airborne Radiometric Snow-Survey System
39 Forensic Neutron Activation Analysis

41 **Atomics International's L-88 Nuclear Reactor for Neutron Radiography** *J. O. Henrie*
41 Reactor Description
43 Neutron-Radiography Parameters
44 **A Radiometric Method for Sulfate Determination** *Edwin H. Klehr*
45 Procedure
45 Calibration Curves
46 Comparison of Methods
48 **Use of Radioisotopic Neutron Sources for Process-Control Activation Analysis** *J. Kuusi*
48 Radioisotopic Neutron Sources
49 Application to Chrome-Concentration-Process Control
53 **Activation Analysis of Particulates**
54 Nondestructive Multielement Analysis of Air-Pollution Particulates *R. Dams, K. A. Rahn, G. D. Nifong, J. A. Robbins, J. W. Winchester*
55 Neutron Activation Analysis of Trace Elements in Airborne Particulates *R. F. Tuttle, J. R. Vogt, and T. F. Parkinson*
56 **A Radiotracer Study of the Acidic Hydrolysis of Poly(Methyl Methacrylate)** *A. B. Robertson and H. J. Harwood*
57 Subsequent Study
57 Experimental
57 Results
58 **Report on Needs for Standard Radioactive Materials**
60 **Radioisotopic Tracer Determination of Flow Rates and Patterns in Tertiary Waste-Water Treatment** *Harry J. Eby and Paul E. James*
60 Test Description
61 Choice of Isotope
61 Test Method
62 Results
63 **Use of ^{14}C in Studying Pollution of the Air by Petroleum Hydrocarbons** *B. Dimitriades*
63 Radioactive Tracer Studies
64 **Isotopes and Moon Rocks**
65 **Atmospheric Tracer Technique Employing ^{85}Kr and Use of This Technique in Defining Puff Dimensions and Transport Speed** *P. W. Nickola, J. D. Ludwick, and J. V. Ramsdell, Jr.*
66 Field System and Data-Handling Techniques
67 Results from Puff Releases
70 Planned Improvements to System

III Food Irradiation

72 **Progress in Commercialization of Irradiated Food**
73 **A German Evaluation of the Significance of Food Irradiation** *L. Wiesner*
74 **Effect of Low-Level Irradiation on Fruit** *E. M. Ahmed and R. A. Dennison*
75 **Radiation Pasteurization of Gulf Shellfish** *F. E. McKinney*
75 Shrimp
76 Oysters

IV Process Radiation Development

78 **Electron Curing of Coatings: State of the Art, 1970** *Allan S. Hoffman*
79 Radiation Considerations
79 Chemical Considerations

80 Curing Mechanism
89 Engineering Considerations
90 Economic Considerations
90 Acknowledgment
92 **Radiation-Initiated Emulsion Polymerization: Pilot-Plant Operation and Economic Feasibility Study (R. S. Allen, J. A. Ransohoff, D. G. Woodard)** *Summarized by R. E. Greene*
92 Pilot Plant
93 Economics
94 **Polymer Grafting to Inorganic Substrates (R. A. V. Raff, R. V. Subramanian, D. J. Schecter, and M. F. Adams)** *Summarized by R. E. Greene*
94 Irradiation of Specimens
94 Experimental Results
96 Glass-Fiber-Reinforced Resins
97 High-Temperature-Resistant, High-Strength Mixed Grafts
98 **Development of a Radioactive-Pebble-Bed Chemical-Reactor System—Phase III (J. Y. Yang, H. T. Cullinan, C. C. Thomas, Jr., and B. F. Ives)** *Summarized by Martha Gerrard*
98 Chemical-Reactor-System Design
99 System Tests
101 **Radiation-Induced Oxidation of Process Effluents at High Pressure** *F. N. Case, D. L. Kau, D. E. Smiley, and A. W. Garrison*
101 Sample-Irradiation Procedures

V Source Development

105 **Isotopic Neutron Sources from the Los Alamos Meson Physics Facility (LAMPF)** *H. A. O'Brien, Jr., and M. E. Schillaci*
106 Description of LAMPF
109 Photoneutron Sources of Interest for LAMPF
112 **Small Irradiator**

VI Applications in Life Sciences

113 **Twenty-Five Years of Isotopes in Life Sciences** *John L. Kuranz*
115 **Role of ^{32}P and ^{33}P in the Synthesis of a Gene**

VII Isotopes Around the World

118 **Use of Radioisotopes in Canada** *Summarized by Martha Gerrard*

VIII Miscellaneous

120 **Availability of Isotopes and Services**
122 **AEC Activities**
124 **General**
125 **Abstracts of Recent Literature**

COVER: Monitoring of radioactive tracers to study wear rates due to abrasion and chemical attack in the bosh area of a blast furnace. See page 16.

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Chairman Seaborg Bids Farewell

Dr. Glenn T. Seaborg has been Chairman of the U. S. Atomic Energy Commission during the entire lifetime of *Isotopes and Radiation Technology*. He has contributed several papers to the Review and has been one of its staunch supporters. In a farewell note, published in the AEC's August 15, 1971, issue of *Rapport*, Seaborg reported, in summing up the decade of accomplishments, that

> Nuclear medicine has become a major means of diagnosing and treating numerous diseases, saving lives and alleviating much suffering throughout the country. A multi-million dollar industry has evolved around the use of radioisotopes in quality control devices that are saving manufacturers significant sums of money as well as assuring consumers better, safer products. Radiation has become a valuable tool of agriculture and promises to become even more important in increasing the world's food supply. Radioisotopes and various nuclear techniques have served as the most sensitive analytical tools in laboratories serving all branches of science and the humanities.

The editors of *Isotopes and Radiation Technology* are pleased to have been involved in reporting these advances and want to thank Chairman Seaborg for his 10 years of strong leadership and to wish him Godspeed. At the same time, we want to welcome his successor, James R. Schlesinger, to the chairmanship and to wish him the very best of everything in his new position.

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United States Atomic Energy Commission (USAEC) reports are available at certain libraries that maintain collections of these reports. The libraries are listed on the inside front cover of each issue of *Nuclear Science Abstracts*. USAEC reports are also sold by the following governmental and international organizations: (1) National Technical Information Service (NTIS), U. S. Department of Commerce, Springfield, Va. 22151; (2) International Atomic Energy Agency (IAEA), Vienna, Austria; and (3) National Lending Library, Boston Spa, England.

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Private-organization reports should be requested from the originator.

The views expressed in this publication do not necessarily represent those of the United States Atomic Energy Commission, its divisions or offices, or of any Commission advisory committee or contractor.

Section

I

Isotopes and Radiation Technology

Isotope Production and Development

Recovery of ^{147}Pm from Savannah River Plant Waste*

Summarized by R. E. Greene

Supplementary Keywords: *production, radioisotope; production, separation; reactor by-product recovery; solvent extraction; chromatography; plant scale; plutonium; ^{147}Pm; ^{144}Ce; ^{146}Pm; ^{148m}Pm.*

Abstract: *Batch solvent extraction procedures were developed for recovering ^{147}Pm, as a mixture of fission-product lanthanides, from the aqueous wastes obtained in processing irradiated nuclear fuels. Extraction of the lanthanides and plutonium with 50% tributyl phosphate (TBP) from concentrated $Al(NO_3)_3$ and/or $NaNO_3$ solution is followed by back extraction into dilute nitric acid. By-product plutonium isotopes are separated from the trivalent lanthanides by extraction, as Pu(IV), into TBP from strong nitric acid. Cerium-144 is separated from the mixture by equilibration of ^{144}Ce(III) with stable Ce(IV) and extracting ^{144}Ce(IV) formed with 50% TBP. Approximately 3 kg of ^{147}Pm was recovered in two plant tests. This is a summary of USAEC Report DP-1236.*

A process for recovering the ^{147}Pm in a lanthanide mixture obtained from irradiated fuels of either natural uranium or alloys of aluminum and uranium enriched in ^{235}U was developed at the Savannah River Plant (SRP).

Promethium has several attractive properties as a possible isotopic power source—2.6-year half-life, which is long enough for many terrestrial and space applications;[1] decay by beta emission only to stable ^{147}Sm; and a maximum bremsstrahlung energy of only 0.224 MeV. Radioisotopic contaminants in reactor-produced ^{147}Pm are ^{146}Pm and ^{148m}Pm, both of which emit penetrating gamma radiation in high abundance. At reactor discharge, fission-product promethium contains ~0.2 ppM ^{146}Pm (half-life 5.5 years) and 5% ^{148m}Pm (half-life 41 days). The ^{148m}Pm decays to an insignificant level in about 2.5 years.

Although several processes have been recorded[2-4] for the recovery of ^{147}Pm, each of these involves steps not compatible with SRP operations. A process reported by Henry[5] for the recovery of americium and curium with tributyl phosphate (TBP) appeared to be readily adaptable to the SRP operations and was therefore evaluated. The adapted process is designed for simultaneous recovery of uranium, neptunium, by-product plutonium, and promethium in a lanthanide mixture (promethium is ~3% of the total mixture) from irradiated enriched uranium–aluminum alloy fuels and natural-uranium fuels.

A brief description of the laboratory separation of promethium, plutonium, and ^{144}Ce and of two plant tests is presented. The separation of neptunium and uranium was described previously.[6]

PROCESS DESCRIPTION

From the solution from which the bulk of uranium and neptunium has previously been separated, the lanthanides (including promethium), residual uranium, and plutonium are extracted into TBP and back extracted from the organic phase with dilute nitric acid containing a reductant for the plutonium (Fig. 1). Plutonium is separated from the lanthanides by solvent extraction with TBP as Pu(IV) from strong nitric acid

*J. T. Lowe, Recovery of ^{147}Pm from Savannah River Plant Waste, USAEC Report DP-1236, E. I. du Pont de Nemours & Co., Inc., Savannah River Laboratory, October 1970.

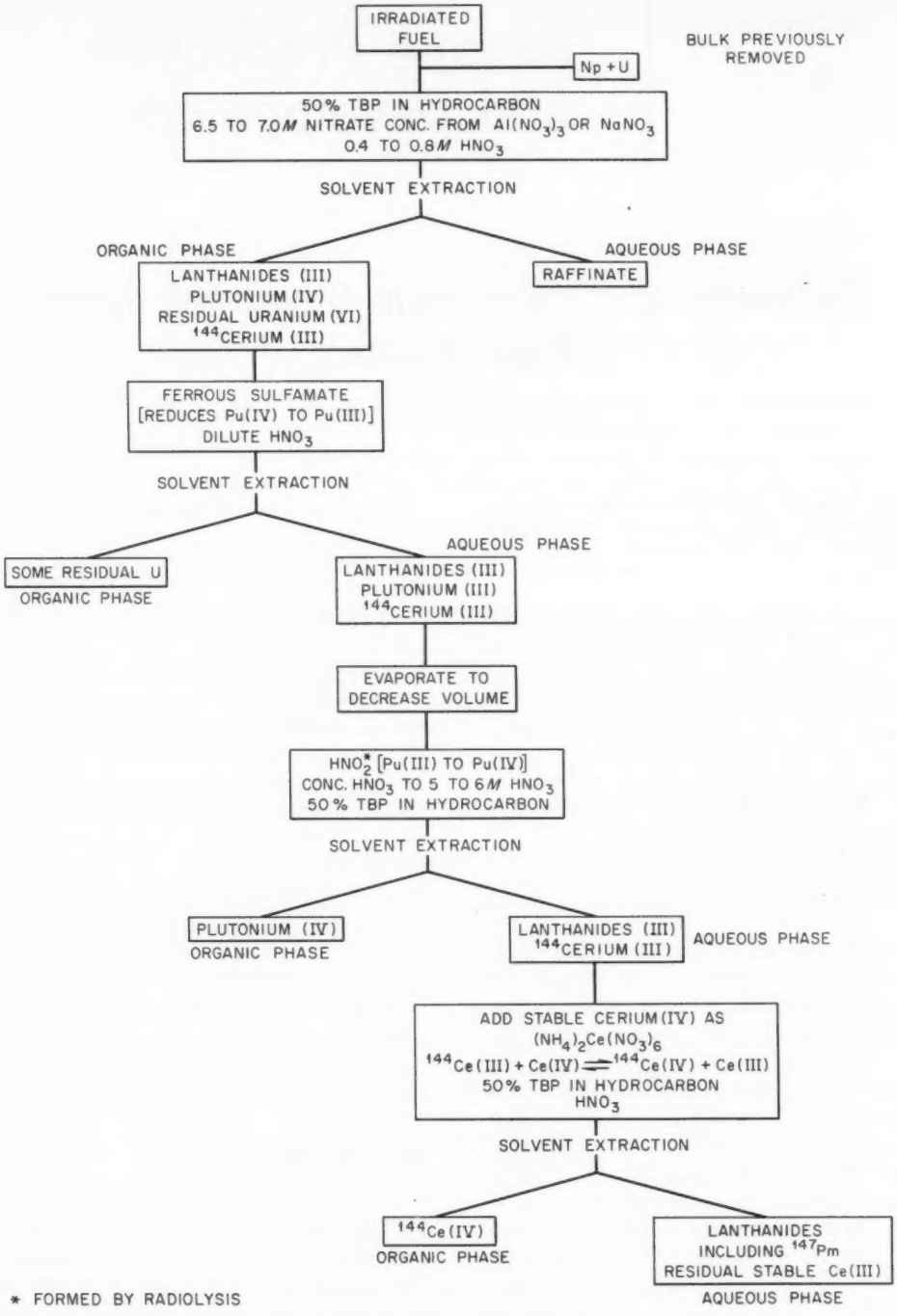

Fig. 1 Flow diagram for the recovery of trivalent lanthanides, including ^{147}Pm, from irradiated fuel.

solution. The most successful method tested for the removal of ^{144}Ce impurity in large-scale separations was exchange of $^{144}Ce(III)$ with stable Ce(IV) and extracting the tetravalent ^{144}Ce thus formed away from the less extractable trivalent lanthanides.

Extraction of Trivalent Lanthanides

In the acquiring of extraction data, ^{144}Ce was used in place of promethium since trivalent cerium is extracted only slightly less than promethium and its determination is much less complicated than that of promethium;[7] extraction data for ^{144}Ce were shown to be comparable to those of promethium. Distribution coefficient data using Ce(III) were determined using various concentrations of TBP in *n*-dodecane, various ratios of $Al(NO_3)_3$ and $NaNO_3$ at fixed nitrate concentrations, and various initial HNO_3 concentrations in the aqueous phase. The conditions for the extraction of lanthanides recommended from this part of the study were: (1) 50% TBP in the hydrocarbon diluent, (2) a nitrate concentration from $Al(NO_3)_3$ or $NaNO_3$ of 6.5 to 7.0*M* (the distribution coefficient increases with an increasing aluminum fraction), and (3) an initial nitric acid concentration of 0.4 to 0.8*M*. Although lanthanides are extracted more efficiently at lower acid concentrations, experience with test solutions showed that lowering the acidity to $<0.4M$ is difficult without adding excess base, entailing the possibility of precipitating lanthanides in the feed solution. The lanthanides and plutonium are easily back extracted into dilute nitric acid.

Separation of Plutonium

Extraction of plutonium from nitrate solution into TBP increases[8] in the order $Pu(IV) > Pu(VI) \gg Pu(III)$. For the back extraction of plutonium with promethium and the lanthanides, the Pu(IV) must be reduced to Pu(III); ferrous sulfamate is the most satisfactory reducing agent. The Pu(III) in the back-extracted dilute nitric acid is oxidized to Pu(IV) with nitrous acid. This solution is then made 5 to 6 *M* in HNO_3 and the Pu(IV) is extracted into TBP. Under these conditions the promethium and other trivalent lanthanides have a very low distribution coefficient.

Extraction of Tetravalent Cerium

In the lanthanides produced by the fission of ^{235}U, the major source of radioactive decay heat is from ^{144}Ce; this heat complicates the subsequent separation of promethium from the other lanthanides. Because of the similarity of the chemical properties of the trivalent lanthanides, the most successful approach for rapid Ce–Pm separation is solvent extraction, which requires oxidation of Ce(III) to Ce(IV) before separation. Tetravalent cerium is almost completely extracted (98 to 99%) by TBP over a wide range of nitric acid concentrations[9] (under the same conditions only 5 to 10% of the trivalent lanthanides are extracted).

Very strong oxidizing agents are required to oxidize trivalent cerium in nitric acid because of its high oxidation potential.[10] Several oxidants were investigated but none was completely satisfactory. The most satisfactory results were obtained by equilibrating[11] stable Ce(IV) with the $^{144}Ce(III)$ in the reaction

$$^{144}Ce(III) + Ce(IV) \rightleftharpoons {}^{144}Ce(IV) + Ce(III)$$

and then extracting the $^{144}Ce(IV)$ into 50% TBP. Tetravalent stable cerium was added as a solution of ceric ammonium sulfate, $(NH_4)_2Ce(NO_3)_6$. Cerium(IV) must be extracted and removed from the organic phase rapidly because TBP is slowly oxidized by Ce(IV), a reaction that is more rapid with radioactive solutions.

Two process variations were evaluated to decrease the effects of reactions of Ce(IV) with the organic phase and with contaminants. The first was the addition of PbO_2 as a holding oxidant (the oxidation rate of PbO_2 is too slow for its use as a primary oxidant). In tests with high-activity-waste solutions, ~85% of the ^{144}Ce was extracted with a Ce(IV)/Ce(III) ratio of 10, and the PbO_2 settled within a few minutes after agitation was stopped.

The second improvement was the use of a miniature centrifugal extractor[12] for rapid phase separation. In feed solutions reasonably free of Cr(III) (from the original raffinate), which reduces the Ce(IV), a centrifugal extractor could eliminate the need for a holding oxidant by reducing the separation time. In a feed solution containing 1260 Ci of ^{144}Ce per liter, 72% of the cerium was removed with a miniature extractor at a Ce(IV)/Ce(III) ratio of ~6.

PLANT-TEST RESULTS

Promethium-147 with associated lanthanides was recovered from waste solutions in two plant tests by batch extraction with 50% TBP, in amounts that agreed well with values predicted from the laboratory studies. In the first test, approximately 500 g of

^{147}Pm in a lanthanide mixture was recovered from accumulated waste solutions generated in the processing of irradiated natural-uranium fuel. In the second test, approximately 2.5 kg of ^{147}Pm—97% of that present in a lanthanide mixture—was recovered from highly active waste from the processing of enriched-uranium fuel. Simultaneously, 95% of the plutonium present was also recovered as a by-product.

Approximately 1 g of ^{147}Pm from the first plant test was used to demonstrate the separation of promethium from other lanthanides by displacement chromatography at high pressure.[13] As part of the feed preparation, ^{144}Ce was separated from the solution using stable Ce(IV) as described and a centrifugal extractor. Seventy percent of the ^{144}Ce was removed. A full-scale plant test for separation of promethium from the other lanthanides has not been conducted.

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Section

II

Isotopes and Radiation Technology

Isotope Technology Development

Report on the Brussels International Conference: Radiation and Isotope Techniques in Civil Engineering, October 28–30, 1970

By George J. Rotariu* and Meyer Steinbergt

Supplementary Keywords: *industry, building; industry, transportation; industry, wood; industry, stone, clay, and glass; polymerization; activation, neutron; activation analysis.*

Abstract: *A summary of the proceedings of a conference on Radiation and Isotope Techniques in Civil Engineering held in Brussels, Oct. 28–30, 1970, is presented. The 400 persons attending the conference heard about 60 papers on a wide variety of subjects. The main emphases were on wood–plastic composites, concrete–plastic composites, and nuclear measurement techniques.*

BACKGROUND

For some time prior to this conference, sufficient radiation and isotope techniques had been developed for application to the building industry or civil-engineering area to permit the planning of a meaningful conference in this field. Accordingly, the first step was taken in January 1970 when G. Pröpstl, Chief, Bureau Eurisotop, Commission of the European Communities (CEC), discussed the possibility of such a conference with E. E. Fowler, Director, Division of Isotopes Development (DID), U. S. Atomic Energy Commission (USAEC). The desirability of holding such a conference was confirmed as was the cooperation of DID in organizing it. Subsequently, at the invitation of CEC, Maso Kato, University of Tokyo, Japan, accepted the coordination for Japanese participation.

The purpose of this conference was to provide an opportunity for scientists and engineers who had developed nuclear techniques for use in civil engineering or in the building industry to present this information to those engaged in these fields. It was hoped that this meeting would provide a stimulus to the building industry and aid and accelerate the use of nuclear techniques. Since the adoption of any new methods by any industry depends on the relative economics of the techniques or process involved, papers on cost analysis and on actual operating-cost experiences with new methods were particularly urged.

The conference was originally planned for 2 days, with a possible maximum of 45 papers. However, 60 papers were received by August 1970, necessitating an extension to 3 days. Actually, even 5 days would not have been toc much, since, with 3 days, 20 papers had to be presented per 8-hr working day.

The conference was held in the auditorium of the Palais No. 7 building, at the Centenaire site adjacent to the famous Atomium structure, in the northwest suburbs of Brussels. The facilities were excellent, not only in meeting the actual needs of the conference but also in providing food and drink, available at all times in the lobby adjacent to the auditorium. Simultaneous translations were provided by CEC in English, French, German, Italian, and Dutch.

About 400 persons from 26 countries attended this conference. The majority of the attendees were European, mostly German and French. Six persons from the United States attended, five of whom

*Division of Isotopes Development, U. S. Atomic Energy Commission, Washington, D. C. 20545.

†Brookhaven National Laboratory, Upton, N. Y. 11973.

presented papers. Very few Iron Curtain countries were represented; Yugoslavia and Romania each had one attendee.

The program and abstracts were printed in the same five languages as the simultaneous translations. However, the papers themselves were printed only in the original language. Copies of all papers were available to the participants at the beginning of the conference.

Opening Session

The conference began with a welcoming address by C. Friz, CEC, who read A. Spinelli's remarks in Italian. Spinelli is the member of CEC responsible for industrial economy, general research and technology, and the Euratom Joint Nuclear Research Centre. This was followed by introductory, welcoming remarks by F. Seynaeve, Ambassador and President of the Committee on Nuclear Energy of the Union des Industries de la Communaute Europeenne, and H. Bouzin, a member of the standing study committee on building-industry problems (building and public works) in the European Economic Community. Introductory remarks by E. E. Fowler, Director, DID, USAEC, stressed the common objective of CEC and USAEC in accelerating the use and application of isotopes in areas of national and international benefit and pointed out that, while many conferences on isotope applications had been held in the past 15 years, this conference was the first international one devoted specifically to the building industry and to civil engineering.

The opening session ended with an excellent presentation by G. Pröpstl, which reviewed the technical aspects of radiation technology for the audience. This provided the reference technical base for the conference.

Conference Sessions and Chairmen

The 60 papers were divided into 13 sessions (see Table 1).

HIGHLIGHTS AND IMPRESSIONS

Three areas were of paramount interest to the authors: the developments occurring in concrete–polymer materials, in wood–plastic composites (WPC), and in nuclear instrumentation technology.

Concrete–Polymer Materials

The interest in concrete–polymer materials is now truly international, and this material is being examined seriously by such countries as Denmark (Risö Nuclear Center and Smith Concrete Industries), France (Conservatome), Japan (Taisei Construction Company and Mitsui–Toatsu Chemical Company), Belgium (S. A. Eternit–Asbestos–Cement Company), Union of South Africa (Rand Mines, Ltd.), and England (U. K. Atomic Energy Authority).

The questions of the cost of making concrete–polymer material and of which curing method to use (radiation or thermal–catalytic) were predominant. K. Singer, Risö, in his paper, indicated a cost of 1.5

Table 1 Sessions and Chairmen

Title of session	Chairman	Title of session	Chairman
Opening	C. Friz (Italy)	Protection of Buildings, Utilities Ventilation (fire protection, lightning conductors, air conditioning, and underground leak detection)	M. Toyer (France)
Mineral-Based Material Combination by Radiation Chemistry (concrete–polymers and polymer–concretes)	C. Friz		
Hydrology	M. Kato (Japan)	Environment of Civil Engineering Structures (waste-water treatment, dust emission from stacks)	G. J. Rotariu (USA)
Industrial Production of Construction Elements and Materials	H. Oel (Germany)		
Control and Regulation on Construction Site	A. Pasta (Italy)	Testing of Civil Engineering Structures (leak detection, gamma-ray radiography of concrete and mortar joints)	F. G. Riessauw (Belgium)
Earthworks, Foundations, Traffic Engineering, Soil Testing	A. Pasta		
Material Combinations Based on Wood and Natural Fibre by Radiation Chemistry (wood–plastic composites)	A. Villiere (France)	Hydraulic Engineering (coastal protection, hydraulic transport, dam construction)	F. Neumaier (Germany)
Testing of Building Materials (non-destructive property measurement)	G. Blom (Belgium)	Radiation Protection in Civil Engineering (construction of shielding walls, natural radioactivity of construction materials, isotope transportation containers)	G. Pröpstl (Eurisotop)

cents/lb for making concrete–polymer pipe; this figure included plant cost and amortization, monomer cost, and radiation-treatment cost. In Denmark, the concrete–polymer pipe would cost about 50% more than ordinary structural pipe.

The thermal–catalytic curing method would appear to have the advantage over the radiation method from two standpoints: (1) it is easier to use in the field, and (2) less shielding, fewer protective measures, and less associated paper work are needed. Further, the thermal–catalytic method can be used at once in any laboratory. However, field conditions (hot weather) and the handling of large amounts of chemical impregnant and catalyst could pose safety problems.

A general feeling of optimism concerning the potential of this new material pervaded the participants. These materials are new from a construction point of view and obviously useful because of various property improvements. The questions raised now are: What are the applications? How much does it cost? Which curing method should be used?

The USAEC-sponsored program in concrete–polymer development was reviewed by one of us (GJR), and recent work by Brookhaven National Laboratory (BNL)–U. S. Bureau of Reclamation (USBR), Denver, was presented by the other. Copies of these papers are available from the authors. The U. S. program is now in its fourth year; three topical reports have been issued.[1–3] The third report was released in February 1971. The U. S. program supports a base program with BNL and USBR to develop the basic information upon which applications development may build. To date, seven government groups and one industrial association (The American Concrete Pipe Association) are involved in formal cooperative programs with the USAEC in developing suitable concrete–polymer materials to meet individual group interest and needs.

Wood–Plastic Composites (WPC)

Recent international developments with wood–plastic composites were covered in five papers: P. R. Hills, UKAEA, Harwell; J. Marchand, CAPRI, Saclay, France; W. R. Green, AECL; R. Pierlas, Conservatome, France; and M. Welt, Radiation Technology, Inc., USA. The English are studying flooring and composite particle board, the French a rather wide variety of woods and impregnants, and AECL has carried out an economic study for the manufacture of WPC. The problem of "end effect," i.e., evaporation of monomer from the ends of the boards, was of general interest as was its possible solution. One group covers the board end with paraffin until polymerization is complete, while another uses pressure on the system to control total evaporation.

The question of the use of WPC flooring in damp areas came under formal discussion. Generally, the usual WPC flooring material cannot or should not be used under moist conditions unless special treatment is given the material to make it impervious to water penetration. One of the organizations present claimed success in this area.

In the informal sessions, the present capability of making WPC commercially was considered more than adequate. While no statements were given on direct annual sales in any country, the present difficult economic times may be a factor in the present slowdown. The potential for WPC flooring is considered to be large.

Associated with this conference was a small exhibit area, where several organizations displayed their WPC materials.

Nuclear Instrumentation Development

In general, the instrumentation techniques presented were types already known to those in the isotope technology field. These included such methods as neutron scattering for moisture measurement (for ground, concrete, and sand); gamma-ray radiography for nondestructive testing of various types of construction materials (steel and asbestos–cement); isotopic tracers for leak detection, flow of groundwater in sites, and wearability of coatings (paints); radiometric density determination for measurement of such things as solid-matter content in waste water, dust emission in cement, steel, and coal and lignite power plants, and density control of roads; and radiometric thickness measurement for quality control of materials used in the building industry.

Applications of X-ray-fluorescence techniques (nondestructive; only X rays impinge on the material being tested; portable), which were one of the main topics of interest at the 1965 IAEA Warsaw conference,[4] have expanded considerably. While this conference had only minimal reference to use of isotope-excited X-ray fluorescence, several papers on the use of neutron activation analysis were given, e.g., the determination of cement content in concrete (^{116}In) and the flow motion of fresh concrete in slurry trench walls (^{153}Sm, ^{46}Sc, ^{198}Au, and ^{122}Sb).

Of special interest, and coming under a very broad definition of radiation, were several papers on laser-beam application to the building industry, all by Siemens AG, Munich; the laser beam was used to

control a rail-aligning machine, a road-laying machine, and a drainage machine.

In general, nuclear instrumentation applications were characterized not so much by the development of brand-new techniques as by the actual application of known methods to specific problem areas in the building industry. That these areas were of interest to the audience was attested to by the fact that there was little attrition in audience attendance throughout the conference.

AVAILABILITY OF INFORMATION

Copies of the program, abstracts, and list of participants may be obtained from Dr. Georg Pröpstl, Chief, Bureau Eurisotop, Commission of European Communities, 200 rue de la Loi, Berlaymont Building, 1040 Brussels, Belgium. State the language desired for programs and abstracts.

The papers presented at this conference will appear in the proceedings, which are scheduled for publication. (RHL)

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Radioisotopes in Blast-Furnace Ironmaking Operations

By W. R. Pavlik*

Supplementary Keywords: *industry, primary metal; measurement, level; measurement, density; material tracing; measurement, moisture; X-ray fluorescence; activation analysis; backscatter; source, neutron; source, gamma; review, technical.*

Abstract: *After providing background material on the blast-furnace process, this article reviews current uses of radioisotopes for on-line analysis of raw materials, raw-materials handling, in-furnace process gaging, process tracing, and quick product analysis. Some possible future uses of radioisotopes are suggested.*

When radioisotopes became available for industrial applications in the late 1940s and the early 1950s, steelmakers were among the first to recognize their value as production and research tools. Advantages such as the ability to "see" through thick furnace walls and perform noncontact measurements in hostile atmospheres provided solutions to previously unsolvable problems. This article will show how steelmakers have taken advantage of the unique properties of radioisotopes and will try to show the direction that future applications may take. This article is the second in a series and will cover only blast-furnace operations. The first article[1] dealt with melt-shop operations. Subsequent articles will cover other phases of steelmaking.

*Electromechanical Research Center, Republic Steel Corporation, Cleveland, Ohio.

THE BLAST FURNACE

Man's use of iron dates back to around 5000 B.C., when iron was not man-made but was recovered from meteorites. Historical evidence indicates that man began to smelt ore to produce iron somewhere around 1500 B.C. Nearly 3000 years later, in the fourteenth century, the first blast furnaces were constructed in

Europe. These furnaces were about 10 to 15 ft high and about 3 to 4 ft in diameter. They produced a few tons of iron per day. Present-day furnaces typically are 100 ft high and have hearth diameters of about 25 ft. These furnaces produce, on an average, 2500 tons of iron daily. A few furnaces have hearth diameters as large as 40 ft and are producing 6000 to 7000 tons daily. Furnaces are already being designed with the goal of 8000 tons/day—a far cry from the few tons per day of the first furnaces!

The importance of correct operation of such giants can hardly be overstated. Approximately one-third of the cost of producing the average finished steel is attributable to the blast-furnace production of iron. Even minor deviations from optimum operating practices increase the cost of iron considerably. More important, the quality of the iron can be adversely affected. To maintain peak production and high iron quality, operators must continually adjust the furnace to compensate for varying raw-material quality and changing furnace conditions. To be effective, adjustments must be based on accurate and timely measurements of these variations.

Unfortunately, there has always been a lack of basic sensing devices that will perform reliably in the harsh environment of the blast furnace. Tracing methods and gages based on radioisotopes have already remedied part of this lack. There remain numerous measurement and control problems at the blast furnace for which radioisotopes may be the solution. In fact, owing to their unique properties, radioisotope methods may be the only answer. Some potential applications are speculated upon in this article.

THE IRONMAKING PROCESS

The first step in steelmaking is the reduction of iron ore to pig iron in the blast furnace. Subsequent steps in steelmaking furnaces refine the pig iron and alloy it with other metals to form steel. Direct reduction processes have been tried to eliminate the blast furnace and produce steel directly from iron ore. However, for a number of reasons, the blast furnace will remain the principal iron maker for some time yet.

Briefly, the ironmaking process is as follows. Iron ore, coke, and limestone are charged in turn into the top of the furnace (Fig. 1). Since the blast-furnace process is essentially continuous, these materials move slowly downward through the furnace, necessitating continual charging to keep the furnace full. Air, heated in the blast-furnace stoves, is blown into the lower part of the furnace through nozzles called tuyeres. The hot air, rising through the materials in the stack, heats the materials and forms a temperature gradient, with the bottom of the furnace being hottest and the top coolest. The hot air ignites coke in the lower part of the furnace stack. The coke provides additional heat for the chemical reactions and for melting the iron and gives off gases which rise through the materials in the furnace stack and reduce the iron ore to iron in the upper and middle regions of the stack. As the materials move down through the furnace stack, the iron ore and limestone soften, and the limestone acts as a flux to remove impurities from the ore. Finally, as the materials enter the bosh (the region just below the mantle), the iron and slag become liquid. A pool of liquid iron 4 to 5 ft deep forms in the bottom of the furnace. Floating on top of the iron is a layer of liquid slag.

About every 4 or 5 hr, the molten iron is drawn off through a tap hole in the side of the furnace. Each tap is referred to as a cast; a typical cast may consist of 400 to 500 tons of iron. The molten iron flows down sand-lined troughs into either a bottle car, for transfer to steelmaking furnaces, or a pig machine for casting into pigs. The molten slag is removed through a separate higher hole prior to the cast; the slagging operation generally occurs more often than the casting operation. The whole process, from the charging of raw materials to the tapping of molten iron and slag, takes between 8 and 12 hr.

The burning coke generates more gases than are used for the reduction of the ore. The excess gases are routed from the top of the furnace, cleansed of dust, and then burned to heat the blast air and also to generate power for running the blowers.

RADIOISOTOPIC ANALYSIS OF RAW MATERIALS

The raw materials used in the blast furnace consist of four major groups: iron-bearing materials, fuels, fluxes, and air. A variation in the chemical composition of these materials will affect control of the blast-furnace process. Radioisotopic-analysis methods can provide an average analysis of a large quantity of heterogeneous material. In many cases, the analysis can be noncontact and can be performed without sample preparation.

Iron-Bearing Materials

Iron for the blast furnace may come from high-grade ores, from beneficiated ores such as taconite,

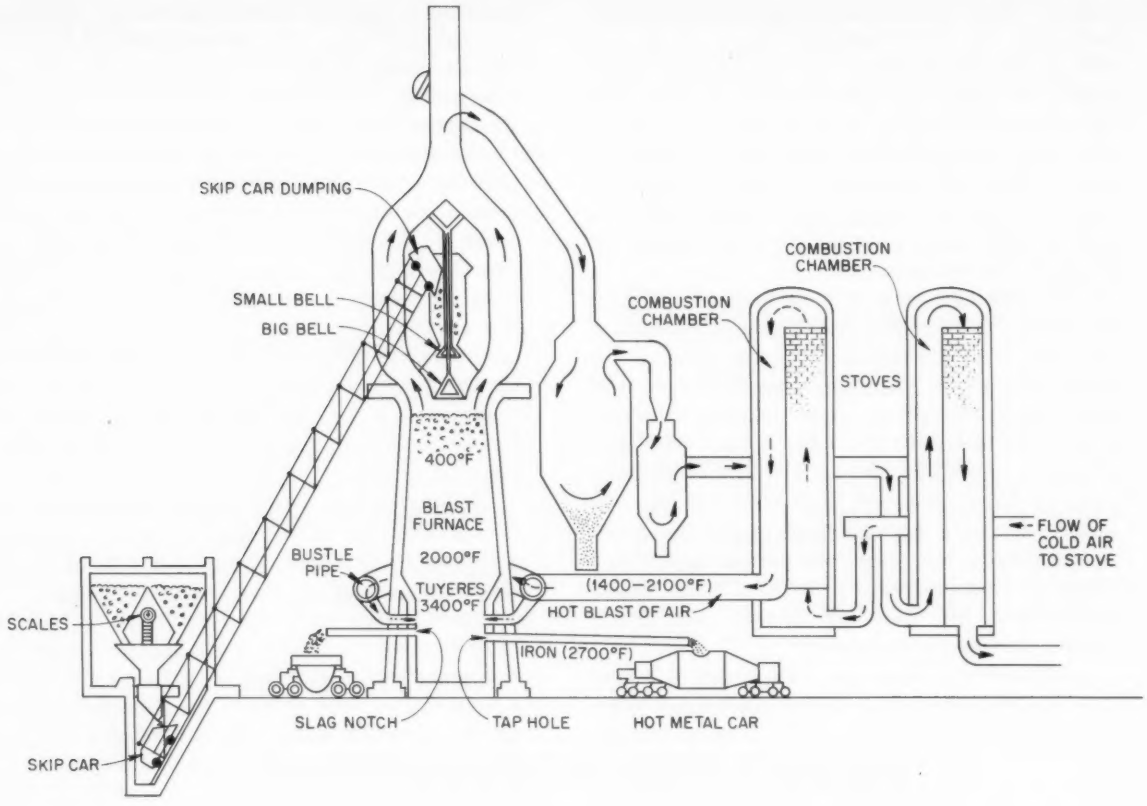

Fig. 1 Diagram of typical material and process flow in a blast furnace.

from sinter, and from scrap. In all these materials, the iron and silicon contents are important factors in producing quality iron. An on-line analysis may someday be performed by either neutron activation or neutron inelastic-scattering techniques. In fact, using both a neutron generator and a ^{239}Pu/Be neutron source, Rhodes[2,3] has analyzed taconite concentrate for silicon both as a slurry and as a solid on a conveyor belt.

Because relatively small amounts of high-grade ore are available, most ore being used is low grade. This ore requires beneficiation to increase the iron concentration, but beneficiated ore is too fine to be charged into a blast furnace and must be agglomerated. The two principal methods of agglomeration are pelletizing and sintering. Sintering is also necessary in order to use such other fines as high-grade ore fines, flue dust, roll scale, coke breeze, and limestone dust. In both pelletizing and sintering, correct moisture content is required to obtain good agglomeration. Reim[4,5] and others[6] have used the principle of neutron moderation by hydrogen as the basis for moisture gages on pelletizing and sintering lines (Figs. 2 and 3). Reim used neutrons from a ^{226}Ra/Be source for measuring moisture and gammas from the source for measuring the weight of material on a conveyor belt. The ratio gives a "moisture per unit weight" signal, which is used to control the amount of moisture being added to the material on the conveyor.

When sintering is used as a reclamation process, the carbon content in the coke breeze and flue dust may vary. A carbon measurement-and-control system will be useful, if not necessary, for a fully automated sinter plant. Stewart[7] tried neutron inelastic scattering as a possible method for measuring carbon in sinter mix and speculated that a measurement accuracy of 0.5% carbon may be possible with an industrial gage.

Regarding other sinter constituents, Booth[8] pointed out that on-line radioisotopic instrumentation for the analysis of CaO and SiO_2 is being developed by

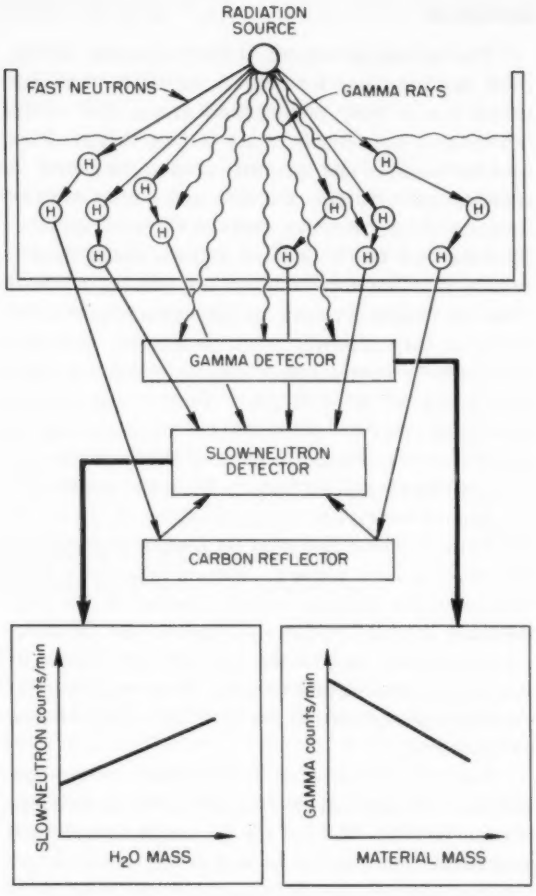

Fig. 2 The neutron thermalization principle used.

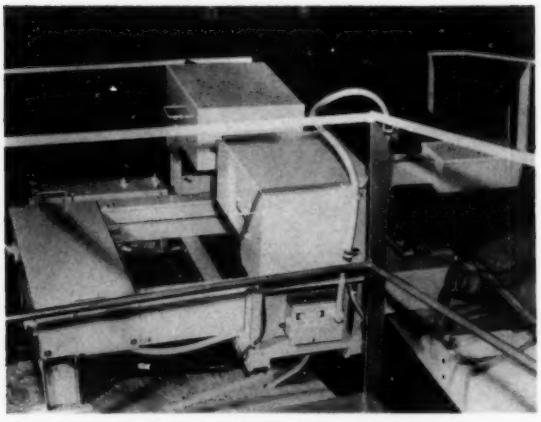

Fig. 3 A nuclear moisture gage on a conveyor line carrying sinter feed material.

the Inter-Group Laboratories of the British Steel Corporation. In 1962, Korzh and Ivanov[9] reported development of a sample method for measuring the iron present in sinter; beta and gamma rays from ^{204}Tl were absorbed by the iron in the sinter, the amount of absorption being proportional to the iron content.

Fuels

The principal fuel for the blast furnace is coke. About 1300 lb of coke is needed for every ton of iron produced. Coke provides both heat and chemical reactants for the reduction of the iron ore. Other fuels (coal, oil, tar, and natural gas) are injected into blast furnaces to reduce coke consumption. Good blast-furnace operation requires that the ratio of coke to ore remain constant. Coke and ore are charged into the furnace by weight. As a result of processing methods, these materials vary in moisture content, which causes weight variations that can lead to serious errors in calculating the coke/ore ratio. The use of taconite pellets has greatly reduced the errors caused by iron-ore moisture variations. However, significant moisture variations in coke continue to be a source of difficulty in properly charging the blast furnace.

Moisture gages based on neutron thermalization by hydrogen atoms are now providing blast-furnace operators accurate data on coke moisture content. With true moisture content known, coke weight can be determined and used in charging the furnace. Coke moisture gages of two general types have been used so far, namely, bin type and conveyor type. The bin types[10–12] are mounted in the coke storage bins, vibrating feeder hoppers, or weigh-car hoppers. The conveyor types[13] are mounted above the conveyor that feeds the coke storage bins.

Another coke property that affects blast-furnace performance is size. Proper size allows blast air to flow through the column of materials in the furnace and aids in the formation of a homogeneous mixture of materials in the furnace. Furthermore, in the bosh area, the drainage of liquid iron through the coke depends on coke size. Polovchenko et al.[14] have described a system that determines coke size by measuring the bulk density of the coke in the weigh hopper just prior to its being loaded into the skip car. The system is based on the attenuation of ^{60}Co gamma rays by the coke in the hopper.

Fluxes

Fluxes are materials charged into the blast furnace for the purpose of removing impurities from the

molten iron. Reactions take place between the flux and the impurities in the ore and coke to form a slag, which floats on top of the molten iron. Limestone is a commonly used flux; dolomite is another. Calcium and magnesium carbonates are the principal constituents of limestone; other constituents include silica and alumina. An on-line analysis for these elements would allow the blast-furnace operator to determine how much of a given flux should be added to the furnace. Perhaps the neutron methods used to determine silicon in taconite concentrate[2,3] could be used to determine silicon in fluxes. Fluorescence X rays excited by ^{55}Fe might provide the basis for an on-line gage that would measure calcium content.

Air

Although not ordinarily thought of as a raw material, air is one of the major raw materials in the blast-furnace process. About 2 tons of air is required for every ton of iron produced. Air has two principal functions in the blast-furnace process: It carries heat from the blast-furnace stove to the raw materials in the furnace, and it plays a role in the chemical processes in the furnace. The CO produced by the burning of the coke acts on the iron ore to reduce it to iron.

The moisture content of the blast air affects the silicon content of the pig iron. Steam is injected into the blast air to compensate for moisture variations caused by atmospheric conditions. Moisture gages based on infrared and visible light are used to indicate the amount of steam that should be injected. Unfortunately, these devices are troubled by a number of inherent weaknesses—they measure the moisture content of samples that may not be representative of the total blast stream, and they require frequent maintenance because of their delicate nature and the severe environment in which they must operate.

An air-moisture gage which is reliable and which can control the amount of steam injected into the blast main is needed. A gage based on neutron thermalization may be the answer.

RADIOISOTOPE APPLICATIONS TO RAW-MATERIALS HANDLING

A typical modern blast furnace uses about 5000 tons of raw materials (not including air) every day. Material must be handled smoothly if the blast-furnace operation is to be efficient. Radioisotopes are already providing significant help and may be the basis of future improvements in raw-materials handling.

Stockhouse

The stockhouse stores correct amounts of ore, coke, and limestone for delivery to the furnace. The stockhouse is built underground at the side of the furnace and is essentially a set of bins that are filled with the various raw materials from ground level. A scale car runs beneath the bins and carries weighed amounts of ore, limestone, and miscellaneous materials from the bins to the skip car. Coke is usually loaded directly into the skip car from the bins by means of vibrating feeders. In some of the newer stockhouses, many of these operations are automated. Radioisotopes already have a role in this automation in such applications as bin-level gages. Future radioisotopes applications may include identification of materials in the bins or the skip car to prevent mixed storage and errors in charging of the furnace. From the stockhouse, the skip car travels up an inclined railway to the top of the furnace, where it dumps its load of materials. A few large-capacity furnaces have recently been built with conveyor-charging systems instead of the conventional skip-car systems. As furnace size increases, conveyor filling may be the only method capable of keeping up with furnace demand. Noncontact nuclear weighing gages are already available for conveyor-borne materials (Fig. 4).

With the advent of conveyor filling, noncontact analysis of all the materials going into the furnace may become possible. Many of the nuclear analytical gages mentioned in this article are well suited to noncontact conveyor gaging. The information from these units could be fed into a computer that would automatically adjust the quantities of various materials being weighed onto the conveyor belt. In this way, the blast furnace could be provided with the best mixture of raw materials.

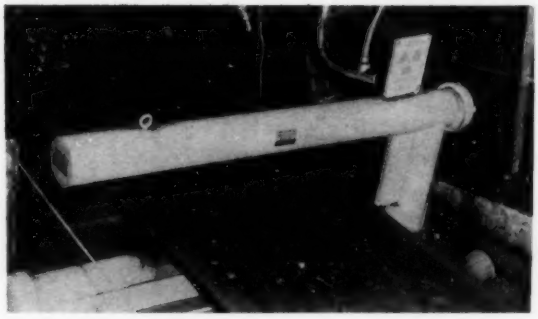

Fig. 4 A nuclear gage for noncontact weighing of conveyor-borne materials.

Furnace Charging

The material carried to the top of the furnace, by skip car or conveyor, is charged into the furnace by a system of bells and hoppers. The material is dumped into a small hopper that has a fitted bottom called a bell (from its shape). When the small bell is lowered, the material falls into a large hopper that has a similar bottom. After several dumpings by the small bell, and with the small bell closed, the large bell is lowered to allow the material to enter the furnace. This system of bells is necessary to maintain a gas seal when material is charged into the furnace. An interesting application of radioisotopes to the small bell, on a conveyor-fed furnace, was reported by Greaves and Ponstingl.[15] A gamma-ray beam scans across the small bell hopper for the purpose of detecting an overfill. When an overfill is detected, the conveyor is automatically stopped.

RADIOISOTOPES IN BLAST-FURNACE PROCESS GAGING

Of all the instrumentation that has been or could be installed on a blast furnace, none can have more direct effect on furnace efficiency than that which measures instantaneously the processes going on inside the furnace. Chemical reactions, temperature variations, and material movements are among the most significant events taking place. Existing instrumentation has been limited by the harsh environment—high temperatures, corrosive gases, and abrasive materials—which prevents the use of most sensing devices. Thick walls of refractory brick and steel provide a formidable barrier for outside-mounted sensors. However, the radioisotope level-monitoring system is one system that overcomes these obstacles and furnishes a significant advance in blast-furnace process instrumentation. Radioisotopes may someday provide ways of measuring the other events taking place within the furnace.

Stock-Level Gaging

For a blast furnace to maintain a high rate of production, it must be kept filled. That is, the raw-material stock level should be as high and constant as possible. The conventional way of measuring stock level in a blast furnace is to lower a weighted rod on a cable into the furnace. The length of cable paid out is an indication of the stock level. This method has the disadvantages of high maintenance requirements and of gas-leakage problems. Nuclear stock-level gages have been developed which use two basic techniques—transmission attenuation and backscatter. Both methods have been tried, with sources and detectors both inside and outside the furnace.

The transmission method uses a collimated beam of radiation from a source on one side of the furnace, which, when the stock is low, is detected on the opposite side of the furnace. When the stock is high, the beam is blocked by the material inside the furnace. Polovchenko et al.[16] used two single source–multiple detector sets inserted into the sides of the furnace. Kruger,[17] Hillnhutter and Kostler,[18] and Wysocki, Buchholz, and Kruger[19] employed single source–single detector pairs in water-cooled tubes inside the furnace. To avoid the difficulties associated with placing the sources and detectors inside the furnace, Stone[20] and Radcliffe[21] developed a system in which the source–detector pairs were mounted on the outside of the furnace shell (Fig. 5). According to Johnson,[22] this type of level gage has proved reliable under production conditions.

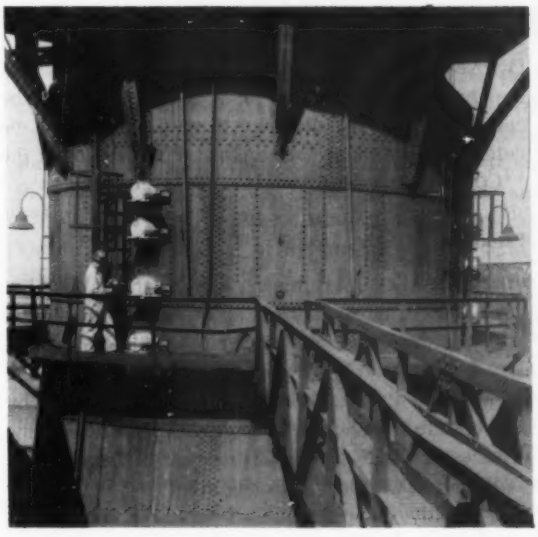

Fig. 5 Radiation sources, part of a radioisotope stock-level gaging system, on the outside of a blast furnace.

The level gages based on the backscatter principle are designed to scan the surface of the burden and determine its profile by use of a movable collimated source and a movable collimated detector. The detector scans the material surface to find the spot of highest intensity backscattered radiation. The azimuths of the source and detector for this spot determine its height and lateral position. Pugachev[23] described a

^{60}Co system mounted inside the furnace; Spooner[24] proposed an externally mounted system.

Top-Gas Analysis

The chemical reactions that take place inside the blast furnace are numerous and complex. A variety of gases figure prominently in these reactions; among these are O_2, H_2, CO, CO_2, and CH_4. A good indication of the processes taking place inside the furnace can be gained from an analysis of the gases at the top of the furnace. Several top-gas analyzers are in use. Like conventional instruments for measuring moisture in blast air, these devices operate on a sampling basis. Their ability to operate properly for extended periods in the harsh environment at the top of the furnace is also questionable.

Radioisotope solutions to the top-gas analysis problem would face the difficulty of interacting with gaseous materials of low density. However, a number of reactions are available for consideration. The fast-neutron method, $^{16}O(n,p)^{16}N$, for determining oxygen in steel might be adapted to top-gas analysis for O_2. Neutron thermalization by hydrogen atoms, which has been the basis for moisture gages, might be considered for H_2 determination. Carbon might be determined by either neutron inelastic scattering or the $^{12}C(n,p)^{12}B$ reaction.

Temperature

Temperature measurement and control in the blast furnace are important for several reasons. Production rates are dependent on temperature, and iron chemistry is considerably affected by temperature. The S, Si, Mn, and P contents of the iron are controlled by temperature. For example, high temperatures in the furnace accelerate the desulfurization of the iron and result in iron with high silicon content.

Presently, temperatures are measured by thermocouples at various locations in the furnace walls and by optical pyrometer readings on the tapped molten iron and slag. Unfortunately, these surface measurements are not indicative of the average temperatures of the great masses of materials and metal in the furnace. Neutrons, which can penetrate deep inside the furnace, may be employed to give a more representative temperature reading.*

*Some consideration has been given to use of gamma backscatter as a surface measurement also. See *Isotopes and Radiation Technology*, 5(2): 121-122 (Winter 1967–1968).—*The Editor.*

Chemistry

Many chemical reactions take place in the blast furnace in the production of iron. The blast-furnace operator can control these reactions better if he has a knowledge of when and to what extent they are occurring. Currently, he has only two sources of information: top-gas analysis and chemical analysis of iron and slag samples. The first is limited to a few elements; the second presents him with information several hours after the fact. The ideal device would "look through" the walls of the furnace and provide a continuous analysis of the product in the furnace. This would make true control of the blast furnace possible. The best possibility of achieving this would appear to lie with the penetrating power of neutrons.

RADIOISOTOPES IN BLAST-FURNACE PROCESS STUDIES

The very first use of radioisotopes at the blast furnace was probably as a tracer to study some part of the blast-furnace process. The blast-furnace process is very complex, and only recently has much been learned about it. Radioisotopes have been used extensively as tracers in the blast furnace because they are uniquely suited for obtaining information from an extremely hostile environment.

Raw-Material Movement

Because raw materials are charged into the top of the blast furnace and the pig iron is tapped from the bottom, a material movement of some 75 to 100 ft must take place through zones of changing temperature and chemistry. Only with a good understanding of the nature of this movement in relation to various operating conditions can maximum production rates be obtained from the blast furnace. A number of investigators[25-27] have used a variety of radioisotopes to study the downward movement of various materials through the furnace. Isotopes that have been used include ^{32}P, ^{59}Fe, ^{60}Co, ^{140}La, ^{141}Ce, ^{192}Ir, and ^{198}Au. In some instances, the radioactivity of the iron and slag products has been monitored. For example, Kohn[28] tagged graphite blocks and lumps of ore and coke with ^{198}Au and ^{140}La and monitored samples of iron and slag. He found that ore lumps required less than 4 hr to be converted into pig iron and slag; coke required about 8 hr to descend through the furnace. In other cases, detectors have been placed at various points on the furnace.

In addition to investigations of the rate of material descent, tracer studies have determined the movement of charge materials in the tuyere zone. Bardin, Gruzin, and Zemskii[29] inserted detectors into the tuyeres to study the movement of tagged materials in that region. They found that materials circle repeatedly from the center of the furnace out to the tuyeres and then back to the center again.

Another radioisotope investigation in the tuyere zone, although not a tracer test and not regarding material movement, was conducted by Smolyak,[30] who inserted a 150-mCi ^{60}Co source in a water-cooled tube through one tuyere and cooled detectors through two adjacent tuyeres. The extent of the combustion zones near the tuyeres was shown by the gamma-ray attenuation.

Liquid-Iron Mixing Studies

Many investigators have used radioisotopes to determine the extent of convection currents in the molten iron and slag in the hearth. If sufficient convection currents exist, iron chemistry and temperature should be uniform throughout a single cast. Kohn[28] used ^{198}Au, which entered the iron, and ^{140}La, which entered the slag. Babarykin et al.[31] used ^{32}P and ^{59}Fe; Mori and Matsuo[32] used ^{60}Co.

Blast-Furnace Chemistry Studies

As better methods for controlling the quality of the raw materials going into the furnace are developed, blast-furnace operators will want to learn more about how the iron chemistry is affected by variations in the raw-material quality. Some of the more important elements in pig-iron chemistry are C, S, Mn, Si, and P. Radioactive isotopes of these elements, introduced as tracers, can show their effects on iron chemistry.

One example of some work already accomplished in this area is the fuel-oil sulfur study by Kusuno et al.[33] The fuel oil occasionally used as a fuel supplement contains a variable amount of sulfur. By using fuel oil with ^{35}S added, Kusuno and coworkers showed that for low-sulfur pig iron, either fuel oils with low sulfur content must be used or the amount of fuel oil injected must be restricted.

Blast-Air Flow-Rate Studies

As far back as 1949, radioisotopes[34] were used to measure gas flow through a blast furnace. Today, the higher wind rates, pressures, and blast-air temperatures used require continued studies with radioisotopes. Leaks, which result in costly loss of blast air and pressure and are a source of air pollution, can be determined by use of radioisotopes at the blast furnace. Radioactive tracers[35-38] have been used to measure the flow rate at various points in the furnace as well as the total transit time through the furnace. Typical tracers have included isotopes of the noble gases Kr, Xe, and Rn.

Refractory Wear Studies

Because of the extreme temperatures inside a blast furnace, the furnace walls must be lined with refractory brick. A significant portion of the cost of producing iron is concerned with this refractory lining. The bricks, the labor for installing the bricks, and the time that the furnace must be shut down during a relining are all costly. Unfortunately, the lining cannot be inspected easily until after it has worn and the furnace has been shut down for a relining. At this time, total wear can be measured, but little can be learned about wear rates, especially those which occur during furnace startup.

Radioisotope-tracer techniques have been used extensively to measure lining wear rates and patterns for different kinds of brick and in different regions of the furnace. Some of the isotopes that have been used include ^{60}Co, ^{65}Zn, ^{110m}Ag, ^{124}Sb, ^{182}Ta, and ^{204}Tl. As a result of these studies, linings now last longer. In some regions of the furnace, thinner linings are now used, resulting in greater furnace capacities.

Tracer tests on furnace linings are conducted in two ways. In both methods, radioactive sources are implanted in different locations in the lining during a relining period. The difference in the two techniques lies in the detection methods. In one method, the sources are monitored from outside the furnace shell. A drop in radiation level signifies the loss of a source due to the wear of the lining. In the other method, the molten iron and slag are monitored; detection of radiation indicates that the lining has worn sufficiently for a source to become detached. The first method provides more exact information on the location from which the source was lost. Also, source intensities can be kept low enough so that the radiation level in the iron is low enough even for such final products as photographic equipment.

Lining-wear-rate studies with radioactive tracers have been conducted in virtually every section of the furnace. Many investigations[39-41] have been conducted in the stack area, where the bulk of the material charge resides prior to melting; most of the wear in this

region is caused by abrasion from the downward-moving charge. Frey[42,43] used ^{60}Co to test the durability of a castable refractory used in repairing the wear-plate area in the stack of a furnace.

Farther down in the furnace, in the bosh area, where reduction of the iron ore and the melting of the iron and slag take place, wear is a combination of abrasion and chemical attack. In 1959, Schepers and Licht[44] reported on a study in this area, and recently Perko and Spirko[45] have conducted extensive tests in this area (Figs. 6 and 7).

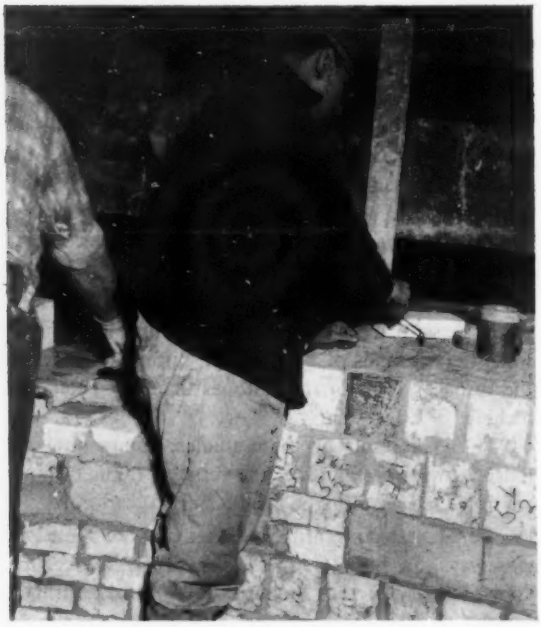

Fig. 6 Radioactive sources being placed in the refractory brick in the bosh area of a furnace during relining.

The bottom of the furnace, where the molten iron rests, is called the hearth and has a lining of graphite or carbon blocks. The Russians[46-50] have studied this area intensively with radioisotopes and report a number of significant improvements in hearth cooling.

RADIOISOTOPE APPLICATIONS TO PRODUCT ANALYSIS

Analysis of the blast-furnace products, iron and slag, is important for two reasons. Obviously, the analysis is needed by the recipient—be it a foundry

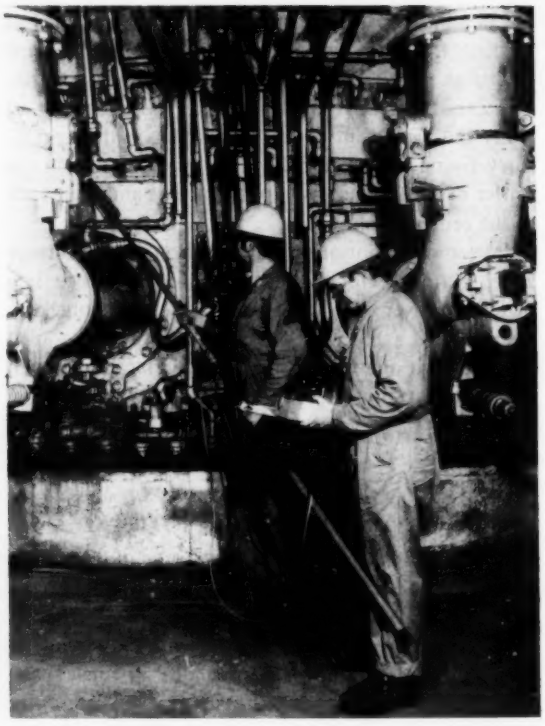

Fig. 7 Monitoring of radioactive tracers to study refractory wear rates in the bosh area of a blast furnace.

that uses pig iron or a basic oxygen furnace (BOF) steelmaking shop. Also, the product analysis is an indication of the blast-furnace performance to the furnace operator. This is particularly important where the operator must alter the procedure because of varying raw-material quality. Conventional analysis methods take time, and during this time the blast furnace continues to produce iron—perhaps off-grade iron. Hot iron going to a BOF can be losing heat while waiting for an analysis, or the BOF can process the iron without an analysis, with the hope that the iron was made to proper specifications in the blast furnace.

A fast analysis method is clearly needed at the blast furnace. Nuclear methods offer the best hope for accomplishing this. Fluorescence X-ray analysis, neutron activation analysis, and neutron inelastic-scattering methods show considerable promise. The initial radioisotopic analysis might be a quick analysis of samples of the iron or slag, with little sample preparation. The next step might be a noncontact analyzer that looks at the molten material flowing from the furnace.

Iron Analysis

The principal properties of iron that are of concern are its chemistry and temperature. The elements of most interest are C, Si, S, and Mn. Republic Steel Corporation is participating in an AEC-sponsored program[51] to evaluate ^{252}Cf as a neutron source for high-speed material analysis.

The temperature of molten iron is of particular importance to the BOF shop. The BOF, which is the prime recipient of liquid iron, requires about a 50% molten-iron charge. The processes in this furnace are quite dependent on iron temperature. Presently, the temperature of the molten iron is measured with an optical pyrometer, which, unfortunately, reads only the surface. The average temperature of the great masses of metal routinely tapped from the blast furnace is not given.

Slag Analysis

Fluxes, such as limestone, are added to the blast-furnace burden to act on the iron ore as purifying agents. These fluxes, along with the impurities they remove, come out of the furnace as slag. The furnace operator can get some measure of furnace performance by observing the composition of the slag. Such slag constituents as MgO and SiO_2 are important process indicators. Conventional analytical methods for magnesium are complicated by the fact that the limestone also carries calcium, which presents a difficult interference for wet chemistry methods. A nuclear slag-analysis method could, perhaps, overcome this difficulty.

MISCELLANEOUS BLAST-FURNACE APPLICATIONS

Radioisotope applications discussed so far have occurred in the process flow through the blast furnace from the charging of raw materials to the casting of molten iron. There are a number of other applications that are not directly related to the main process flow.

Raw-Material Preparation

Radioisotopes have been used as tracers to study the preparation of materials used in the blast furnace. Taconite pellets are prepared by crushing raw taconite, concentrating the iron content magnetically, and pelletizing the concentrate. One of the crushing methods is a ball mill. Stone[52] used tracers to determine the wear patterns and wear rate of the steel grinding balls (Fig. 8). A few balls were irradiated and placed in the mill along with thousands of unirradiated balls. Periodically, the irradiated balls were located with radiation-detection instruments and recovered for weight and geometry measurements. Tracers might also be used to study the dynamics of other crushing methods, the magnetic separators, or the pelletizing operations.

In 1968, Russian workers[53] reported on tracer experiments designed to measure the efficiency of a primary mixing drum in a sintering plant. Isotopes used were ^{32}P, ^{95}Zr, and $^{55,59}Fe$. The quality of mixing depended on the degree of fullness of the drum, the material-size grading, and the moisture content.

Gas Cleaning

The gases coming from the top of the blast furnace are used as fuel for firing the blast-furnace stoves and other equipment, such as boilers and coke ovens. These gases are heavily laden with dust, which, unless it is removed, would quickly clog this equipment. Bulba and Wallace[54] have tested a device, based on a beta source, for monitoring the dust content of the cleaned blast-furnace gas in the gas main just ahead of the blast-furnace stoves.

Dust Catcher. The blast-furnace gas is routed from the top of the furnace through four vertical pipes called uptakes, then downward through one or two inclined pipes called downcomers into the gas-cleaning equipment. The gas-cleaning equipment consists of a dust catcher, a set of gas washers, and electrostatic precipitators. The dust catcher is a large vertical cylinder, cone shaped on both top and bottom, in which the larger dust particles fall from the gas and collect. Periodically these particles are dumped from a bottom gate into a truck or rail car. Radioisotopes have been used to determine[55] the rate of dust accumulation in the dust catcher; ^{60}Co wires were placed in the center of the dust catcher, and radiation levels were monitored at various locations around the outside. Dust-level gages[56] have also been installed to give continuous indications of the dust-accumulation rate.

Pipe Deposits. Throughout the gas-handling system, dust deposits can form on the insides of pipes. In the past, the only ways of determining this dust buildup were by observing the diminished flow of gas or by opening sections of pipe for inspection. The first method does not tell where a buildup is occurring; the second method has the obvious disadvantages of interruptions of operations and large labor expendi-

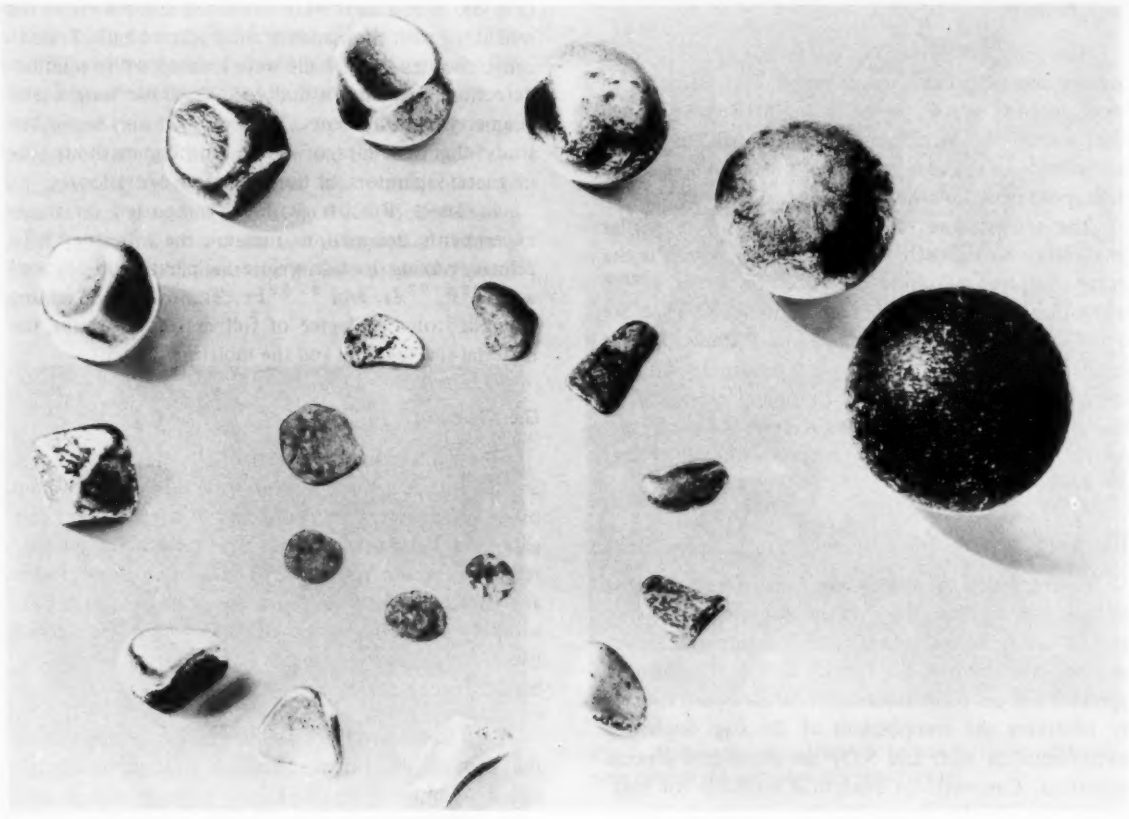

Fig. 8 Wear rate and pattern of a grinding ball from a ball mill (new ball shown at right).

tures. Radioisotope techniques can be used to measure deposits from outside the pipe without interrupting operations.[57] Either gamma-ray transmission attenuation or backscatter approaches may be used, depending on the particular installation.

Dust-Rate Studies. The foregoing discussions covered techniques for measuring dust-accumulation rates and efficiencies of gas-cleaning equipment. Some investigators have attacked the problem at its source by using radioactive tracers to determine the dusting rates of various materials. Because high-quality iron ores are in short supply, low-grade ores and reclaimed iron-bearing materials are being charged into the blast furnace in the form of pellets and sinter. One measure of the quality of the agglomeration is the amount of dust that is blown through the furnace and trapped in the dust catcher. Von Bogdandy and Schmolke[58] used a tracer technique to compare the dust rates of sintered briquettes and cold-compacted briquettes. They found that 13.5% of the cold-compacted briquettes was blown out of the furnace as dust, whereas the sintered briquettes had a dust rate of only 4.5%. Similar experiments[52] have measured the dusting rate of taconite pellets. The pellets were irradiated, and the ^{59}Fe resulting from the irradiation was used as the tracer (Fig. 9).

Pollution Monitoring

Today there is increased concern over the effects of both air and water pollution on the environment. The steel industry is faced with vast expenditures of money and effort to make sure that it will not be a contributor of pollution. Radioisotopes can make a significant contribution to the pollution-control program. For example, short-half-life tracers can be used to determine the sources of gas and dust leaks from the blast furnace and to measure the effectiveness of waste-water treatment facilities. Short-half-life isotopes

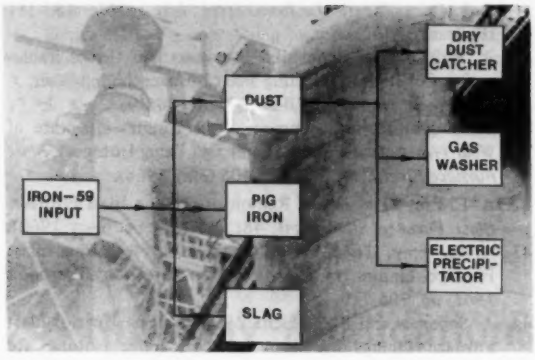

Fig. 9 Schematic flow of radioactive iron (^{59}Fe) shows locations of blast-furnace dust losses.

have the advantage of not being contributors, in themselves, of radioactive pollution. Radioisotopes might also be used in instruments for monitoring the discharges into the air and waterways for possible pollutants.

CONCLUSION

This article has covered both the existing and potential applications of radioisotopes to all areas of the blast-furnace process—from raw-materials handling and processing, through the furnace itself, to the final product. An attempt has been made to show as many diverse existing applications as possible and to give a glimpse of some future applications. With the proper facilities, trained manpower, and dedication, these potential applications can become reality.

(FEM)

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Highway Applications of Nuclear Techniques*

Summarized by P. S. Baker

During 1970, the Highway Research Board Committee A2-HO1 (concerned with nuclear principles and applications) contacted the 50 state-highway departments of the United States concerning the possession and usage of nuclear equipment for surface testing with the intent of determining the current status of nuclear testing. Table 1 and Fig. 1 summarize these findings.

It is of interest to note that *all* of the state-highway departments at one time or another have used nuclear testing either in research or for field control, or both. California, Pennsylvania, and Virginia are the three leading states in numbers of gages used for moisture–density testing on soils and aggregates, with 137, 125, and 102 devices, respectively.

Table 2 shows the growth of nuclear gaging as far as highway applications are concerned.

*From Highway Research Board Circular No. 121, Highway Research Board, Washington, D. C., February 1971.

Fig. 1 Nuclear systems in use by state-highway departments in 1970 for surface moisture–density testing.

Table 1 Use of Nuclear Systems for Surface Testing by U. S. Highway Departments

State	Moisture–density systems for surface soils and aggregates	Systems used for asphalt density	Asphalt-content devices	Moisture–density specification control for soils and aggregates	Asphalt-density specification control
Alabama	12	1	0	12	0
Alaska	6	1	1	6	0
Arizona	14	14	0	0	12
Arkansas	1	0	0	1	0
California	137	1	0	137	0
Colorado	28	21	1	28	21
Connecticut	9	5	0	0	0
Delaware	11	11	0	0	0
Florida	26	2	1	25	0
Georgia	14	1	0	14	0
Hawaii	2	0	0	0	0
Idaho	3	1	0	0	1
Illinois	26	4	0	26	4
Indiana	10	4	0	2	4
Iowa	3	0	0	0	0
Kansas	5	3	2	0	2
Kentucky	15	0	0	15	0
Louisiana	40	0	0	40	0
Maine	2	0	0	2	0
Maryland	5	1	1	4	0
Massachusetts	1	1	0	0	0
Michigan	7	1	0	0	0
Minnesota	2	1	0	0	0
Mississippi	8	0	0	3	0
Missouri	1	0	0	0	0
Montana	49	2	2	49	0
Nebraska	3	1	1	0	0
Nevada	3	0	0	1	0
New Hampshire	1	1	0	1	1
New Jersey	4	1	0	0	0
New Mexico	10	5	0	0	0
New York	1	0	0	0	0
North Carolina	3	1	0	3	0
North Dakota	16	15	0	15	15
Ohio	34	2	0	34	0
Oklahoma	2	0	0	2	0
Oregon	1	1	0	1	0
Pennsylvania	125	31	2	123	0
Rhode Island	5	1	0	4	1
South Carolina	1	0	0	0	0
South Dakota	15	11	0	0	11
Tennessee	12	4	0	11	4
Texas	9	1	0	5	0
Utah	32	35	2	32	35
Vermont	2	0	0	2	0
Virginia	102	100	1	100	100
Washington	1	0	0	0	0
West Virginia	22	25	1	20	20
Wisconsin	24	8	0	18	8
Wyoming	16	9	0	0	0
TOTALS	881	327	15	736	239

Table 2 Use of Nuclear Applications by U. S. Highway Departments

	1962	1964	1967	1970
U. S. highway departments engaged in nuclear testing	56	74	94	100
Nuclear testing used for specification materials control, %	14	24	56	70
Nuclear testing used for density determinations of asphaltic pavements, %	0	22	54	72
Total number of systems used	0	19	126	327

Neutron Activation and On-Stream Analysis in the Mineral Industries Using SHERLOCK III*

By K. V. Godfrey† and W. E. Downs‡

Supplementary Keywords: *activation analysis; activation, neutron; source, neutron; industry, mining; chemistry, analytical; pilot-plant scale; spectrometry; hafnium; copper; molybdenum;* ^{124}Sb.

Abstract: *The SHERLOCK III neutron irradiator is a simple, safe neutron activation unit that generates a neutron flux of* 10^8 *n/(cm²)(sec) by the* $^{124}Sb(\gamma,n)$ *reaction in beryllium. The irradiator, which can be used either for continuous on-stream analysis or for batch irradiations, is described, and some applications of the unit in the continuous analysis of ore slurries in the mineral industries are discussed.*

The increasing need to exercise better control over ore mill circuits has resulted in a requirement to develop rapid, accurate methods of measuring circuit variables. One of the most important of these is the assay of the material in the circuit (or about to be introduced to the circuit). To date, most on-stream analysis has been performed using X-ray-fluorescence (XRF) equipment.

Neutron activation analysis (NAA) offers an alternative method in certain circumstances, with several interesting advantages. Recognizing the need for a simple, safe neutron activation unit suitable for on-stream analysis in the mineral industries, Atomic Energy of Canada Limited (AECL) has designed, built, and tested the SHERLOCK system. One prototype (SHERLOCK I), in Ottawa, is used primarily in research. A second prototype (SHERLOCK III), in Vancouver at the laboratories of B.C. Research, is being used for some development research and for evaluating the unit for specific applications.

Most of the work completed to date has been aimed at proving the technique and at developing some of the factors needed to design systems for milling plants.

Several sources of neutrons are currently used for activation analysis. At the most powerful (and expensive) extreme of the range are the small nuclear reactors. These offer little potential to the mining industry for on-stream work, primarily because they are expensive and require highly skilled operating personnel. Advances in technology may make the small reactor more feasible in the future.

Next are the neutron generators that produce high fluxes over relatively small areas. In the past, generators have been used only in the laboratory, but again developments in technology are making these units available for on-stream work.

Finally, isotopic sources of neutrons offer the conveniences of ease of use, robustness, and a relatively low price. The "two-element" sources, in which a radioactive element acts on a passive element to

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† Research Officer, B.C. Research, Vancouver, B. C.

‡ Commercial Products, Atomic Energy of Canada Limited, Ottawa, Ontario.

produce the neutrons, have been used extensively, particularly in the oil industry for neutron logging. Among active elements that have been used are Ra, Pu, Am, and Sb with Be as the passive element. SHERLOCK belongs to this third category.

Each source has its own peculiar advantages, and this article makes no attempt to examine relative merits, since recent reports[1-3] deal with this subject in much greater detail. Rather, one source type—the isotopic ^{124}Sb–Be—and some of the experience with it will be described.

DESCRIPTION OF SHERLOCK III

SHERLOCK III is a neutron activation unit developed by AECL in Ottawa, Canada, and installed in the laboratories of B.C. Research, Vancouver, Canada. Figures 1 and 2 illustrate its simplicity. The total operating weight of the unit (including transfer case) is 32 thousand lb, with a floor loading of 2000 lb/ft^2. The irradiation unit consists of a ^{124}Sb source with its source transfer case, a cast-iron shield, a radiation chamber, and a moderator circuit.

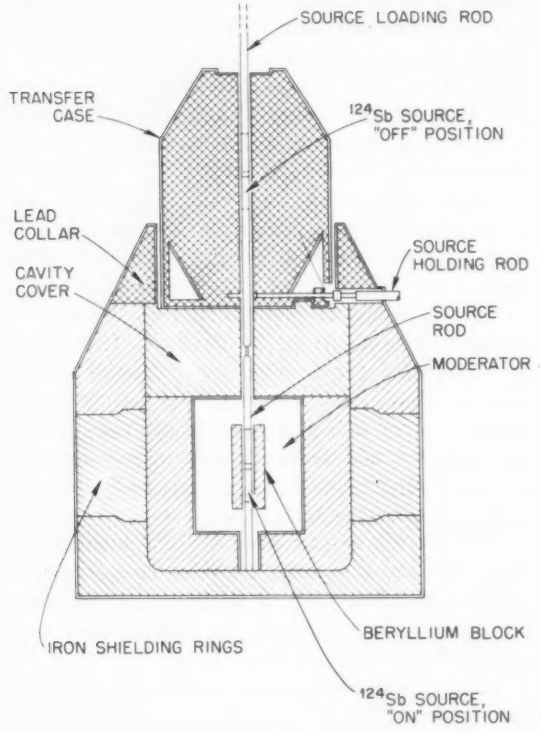

Fig. 1 SHERLOCK III configuration.

Fig. 2 SHERLOCK unit assembled.

The ^{124}Sb source and source transfer case component is constructed in such a way that the source and case are never separated except during a source exchange at AECL. The case, when used in conjunction with the special fire shield and shipping crate, is designed to comply with the Atomic Energy Control Board shipping requirements, and shipment of a fully charged source is permitted. The total weight (transfer case plus shipping crate) is 5800 lb.

The transfer case is equipped with safety locks to prevent accidental removal of the source. On arrival at the SHERLOCK unit, the transfer case is mated with the basic unit, permitting the source to be lowered into the beryllium block (Fig. 3). The case is an integral part of the shielding and is never removed from the unit while the source is in the lowered position.

The cast-iron shield is in four parts: a base, a center ring, a top ring, and a cavity cover. The weight of each of these items is ~6 thousand lb. The cavity cover contains two independent slurry–liquid flow lines for on-stream analysis, two pneumatic rabbit systems for discrete sample analysis, and the moderator circuit lines. This gives 10 separate lines that have to pass

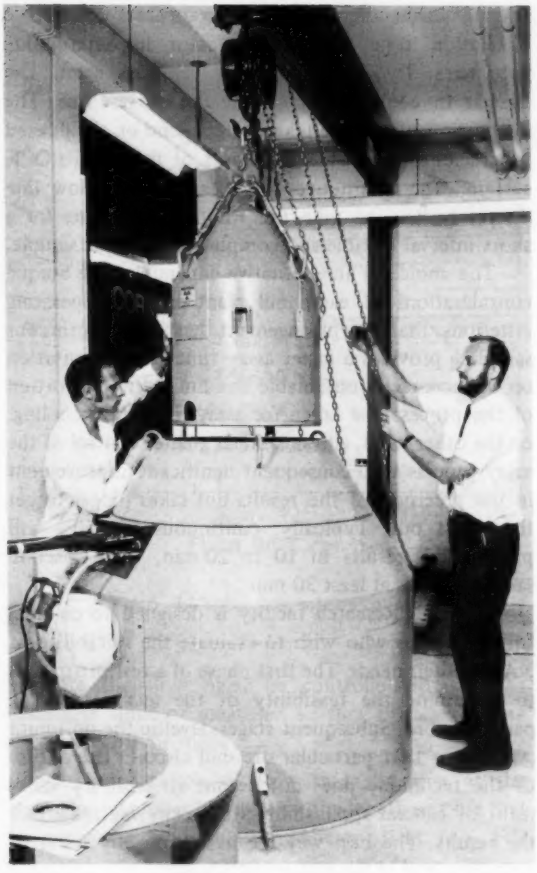

Fig. 3 Installing source transfer case on SHERLOCK body.

through the cavity cover without permitting an escape of neutrons. This machining is the most complex part of the unit. A lead collar completes the shielding.

The shielding described above surrounds a cavity or chamber where the neutron flux is produced. The chamber contains a moderator can that holds distilled water and in which is suspended the beryllium block. The slurry–fluid sample chamber surrounds the beryllium block and is contained in the moderator can. The two pneumatic rabbit sample lines terminate in the top of the beryllium block.

The moderator circuit includes a pump, a deionizer, and the necessary piping.

PRINCIPLE OF OPERATION

The neutron source has two parts, a beryllium block and the ^{124}Sb. When the two are separated, no neutrons are produced, and only gamma-ray shielding is required for the antimony. When the ^{124}Sb is lowered into the center of the beryllium block, neutrons are produced by a (γ,n) reaction.

The water, which is purified to prevent corrosion and to eliminate impurities that might capture neutrons, is used as a reflector and moderator to convert the neutrons to thermal energies. A flux of approximately 10^8 thermal neutrons/(cm^2)(sec) is obtained from this reaction. The ^{124}Sb has a half-life of 60.2 days. Source replenishment will depend on specific applications, but the frequency required is not likely to be more than once every 3 months. In fact, many applications may permit a less frequent source change.

Sample Systems

The SHERLOCK III unit provides two independent fluid sample lines. Both lines enter through the cavity cover via 0.5-in.-ID stainless-steel lines and terminate inside the irradiation chamber with 0.5-in. Swagelok fittings. The fluid is directed around the beryllium block in a suitable container. The size and construction of the container depend on the nature of the material being assayed and the user's requirements. Usually it consists of a coil of tubing on an annulus surrounding the beryllium block. Pumps, piping, and sampling devices are not considered as part of the unit.

The design provides for the irradiation of solid samples without interruption of the continuous-flow analyzer, provided separate counting facilities are available. Samples of the material are placed in 2- by 1-in.-diameter capsules and are blown by compressed air into cavities inside the beryllium block through a stainless-steel tube encased in the cavity cover. Two such lines are provided. This rabbit system operates from a 50-psig air supply either manually or automatically. Solid-state control units can be used that provide automatic sequencing and timing of the irradiation and counting functions.

Counting Equipment

The gamma rays emitted by the radioactive isotopes induced during irradiation are counted, using standard equipment. Typically, a setup will include a suitable shield to protect the counting equipment from background radiation; a means of detecting radiation, amplifying the detected signal and converting it to a digital value; and a unit to count, store, and display the resulting information.

Figure 4 shows a cross section of the counting chamber at B.C. Research. The chamber can accom-

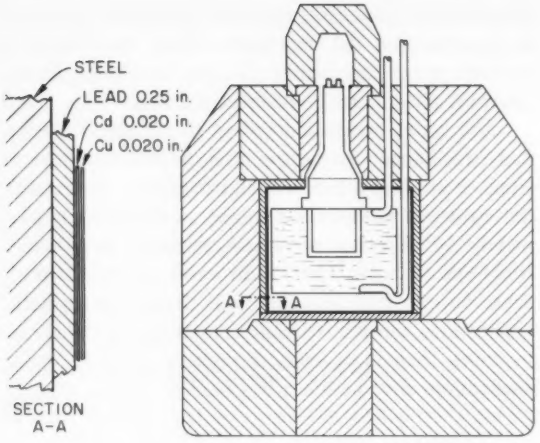

Fig. 4 Cross section of counting chamber.

modate two 5- by 4-in. sodium iodide detectors complete with their multiplier phototubes. The configuration of the counting chamber itself is again dependent on the specific material being analyzed. A Hewlett–Packard $x-y$ plotter and a parallel printer are used to record the data, and data are reduced on either an IBM 1800 or an IBM 360/67 computer. The setup at B.C. Research is designed to facilitate research, development, and testing; an actual operation may not require the same degree of sophistication.

MILL-CIRCUIT CONSIDERATIONS

Control of a mill circuit is based primarily on determination of the major mineral constituents in the mill feed and in the various mill products. Several points must be considered in effecting this control.

Total continuous analysis of the mill streams would eliminate the major problem of sampling and would present perfect data on which to base control. However, economics will probably enforce a compromise. If the size of the sample can be increased, the relevance of the assay to the mill circuit will be substantially improved. Neutron activation is a volumetric technique in which the neutrons penetrate deeply and the subsequent gamma rays can be counted through many thicknesses of material. These considerations indicate that NAA has the potential to effectively increase the sample size.

In SHERLOCK, the volume of sample assayed depends on the size of the irradiation chamber. Typically, this container can hold 1 to 3 imperial gallons of slurry. This volume is usually not large enough to handle the complete process line, since irradiation time is a major factor in determining accuracies. Two possibilities for sampling exist. The first is to continuously sample the process line. The proportion of the line taken will depend on the desired accuracies and flow requirements of the SHERLOCK system. The alternative is to sample the flow line discretely, i.e., to take the whole process line for a short interval of time and completely assay the sample.

The choice of an alternative depends on the unique considerations of each mill plant and the operating criterions that its management has set. Continuous sampling provides a faster assay time with a limitation on the accuracies obtainable but limits the proportion of the process line taken for assay. Discrete sampling, on the other hand, allows a much greater control of the assay process with consequent significant improvement in the precision of the results but takes longer to get the result out. Typically, continuous sampling will provide the results in 10 to 20 min, while discrete sampling takes at least 30 min.

The B.C. Research facility is designed to do tests for companies who wish to evaluate the suitability of NAA to their needs. The first phase of a test program is to determine the feasibility of the technique on a particular ore. Subsequent stages develop the optimum system for that particular ore mill circuit. The nature of the technique does not permit an arbitrary statement of general applicability; too many factors affect the results. The best way to investigate any ore is to actively test it in the SHERLOCK unit.

RADIATION VARIABLES FOR AN ON-STREAM NAA CIRCUIT

When on-stream analysis work using NAA is being considered, a number of general variables are important. The chemical elements of interest in the circuit must first be defined, and then the major interferences, the total time between sampling and when the information is to be made available, and the accuracy required are considered.

The first variable that affects the results is the flow rate. When a proportion of the main line is being sampled, the flow rate is often governed by the circuit and settling considerations and not by nuclear requirements. Figure 5 shows the variation of the counts with flow rates for two typical elements. For the long-lived isotopes (^{24}Na), the slower the flow rate, the higher the count rate; and for short-lived isotopes (^{28}Al), an optimum flow rate exists. Variations in flow rate can obviously affect the accuracy of the final result;

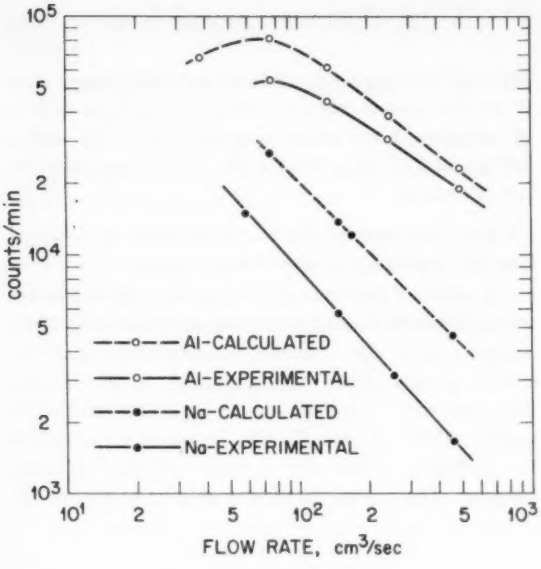

Fig. 5 Effect of flow rate on counts.

therefore the flow must be controlled to within a reasonable limit or measured so that the appropriate corrections can be made.

The combination of flow rate and size of the irradiation chamber will govern the length of time that the elements stay in the neutron field (t_i). For long-lived isotopes, a long irradiation time can be achieved in three ways: (1) slower flow rate; (2) larger irradiation chamber; and (3) cycling the sample. A practical limit to how slowly a sample can be pumped is imposed by the settling characteristics of the slurry. The flux drops off as the sample moves away from the source, and a 3-gal chamber is the largest size that will make any improvement in the results. For larger chambers, the decrease in flux offsets any increase in irradiation time. When a longer irradiation time is needed, the cycling or batch system can be used.

Once the sample leaves the irradiation chamber, there is a finite delay in moving it to the counting chamber. This time interval is designated as the delay time, t_D. For a single element with a fairly short half-life, this time should be the minimum that is physically possible. This delay time may be used to advantage by allowing interfering elements to decay. A typical example might be a combination of ^{24}Na (15 hr) and ^{28}Al (2.3 min). A 10-min delay would reduce the aluminum to a reasonably low level, while the decrease in sodium would be barely detectable.

Once the sample enters the counting flow chamber it contributes counts to the detector as long as it is in the chamber. With a large chamber, the efficiency of counting will vary considerably depending on the location within the chamber. However, a properly designed chamber should average this effect as the sample passes through. The two main variables connected with the counting chamber are the Compton scatter found under the various peaks and the total counting time.

Compton scattering is a function of the chamber thickness and the density of the material in the chamber. The thickness and size of the chamber are variables controlled by the designer. B.C. Research is now working to show the effect of density on Compton scattering.

Increasing the counting time, t_C, allows for improved accuracy and sensitivity but delays the total analysis time and increases the amount of material that is being averaged. A 10-min count time on a stream moving at 1 gal/min will average the results over a 10-gal sample. In nuclear work, one of the main considerations in any measurement is the counting accuracy, which is based on the statistics of nuclear decay. A $\pm 2\,\sigma$ error value is obtained by doubling the square root of the total count in time t_C. Therefore by doubling the counting time the sensitivity can be improved by a factor of 2 or the accuracy by a factor of 1.4.

RESULTS

A prototype SHERLOCK system has been in operation for almost 2 years. A number of preliminary studies have been done using industrial and synthetic solutions. One such study is reported in detail to illustrate the problems encountered and the data manipulation required when this technique is used. Some of the other possible applications studied with the prototype are mentioned briefly.

The application is the determination of hafnium in a zirconium concentrate in a 2*M* solution of HCl. The client's requirements called for determination of 0.5 to 30 ppM hafnium on a solution basis with an accuracy of ± 10% and an analysis time of 10 to 15 min. Forty-five gallons of the industrial solution were obtained for this experiment, and the SHERLOCK I prototype was fitted with a 1-gal irradiation chamber. A 0.34-gal delay line, a 0.12-gal counting chamber, and a flow rate of 1.6 gal/min were used. The delay line gave a 12-sec delay to eliminate the 0.74-sec half-life ^{38m}Cl peak.

The basic spectrums obtained from these runs are shown in Fig. 6. Because the chlorine peaks are of a higher energy than hafnium, they will interfere with the hafnium data and must be accounted for. However,

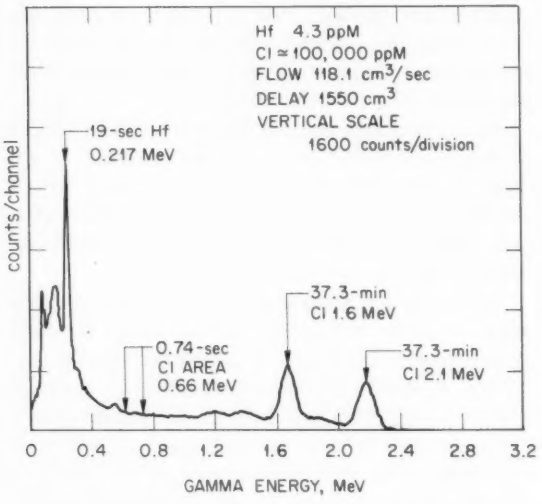

Fig. 6 Spectrums of Hf and Cl with the ^{38m}Cl removed by delay-line increase, Run No. 3.

high-energy interferences can be corrected for rather simply: With a fixed geometry system, the percentage of Compton scatter appearing in the hafnium peak and originating in the two chlorine peaks will be constant or nearly so. This ratio is designated as K and is defined as the ratio of chlorine Compton counts in the hafnium area to the gross chlorine counts under the two chlorine peaks. If this ratio is measured for any given counting geometry, it can be used in later data-reduction work to account for the chlorine interference in the hafnium area. Thus counts due to hafnium only can be calculated from the following equation:

$$Hf_0 = T - B - KY \qquad (1)$$

where T is the integrated gross counts in the hafnium area, B is the background counts in the hafnium area, and Y is the integrated gross counts in the chlorine areas.

Equation 1 must be corrected for the decay of ^{124}Sb and must also be calibrated in order to indicate parts per million of hafnium. Thus Eq. 1 becomes

$$Hf_0 = G\,(T - B - KY)/\exp\,(-\lambda t) \qquad (2)$$

where G is a previously determined calibration factor to convert counts due to hafnium to parts per million of hafnium, λ is a decay constant for ^{124}Sb with a half-life of 60.2 days, and t is the time in days since the last calibration.

This data manipulation can be done in a special electronics package or in a small computer.

A series of runs was made to determine the effect on net hafnium counts of such variables as the hafnium concentration, the chlorine concentration, and the specific gravity of the sample solution. In all runs, the flow rate was 1.6 gal/min ± 1%. Variations in specific gravity affect the ratio K (Fig. 7), which is partly due to scattering within the solution in the counting chamber. This means that if the specific gravity of the

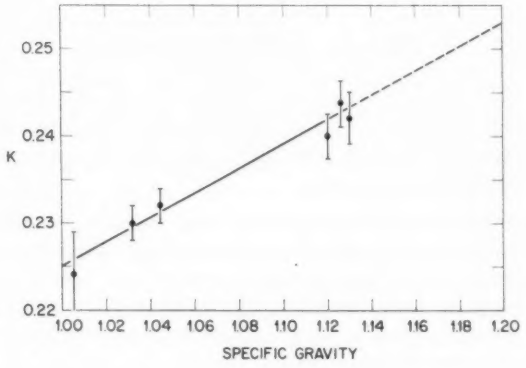

Fig. 7 Variation of K with specific gravity.

solution varies, the ratio K must be corrected before the hafnium concentration can be calculated. Chlorine concentration is very high in this solution (i.e., 10^4 ppM), and, because the chlorine is absorbing neutrons through activation, it tends to depress the flux. Since chlorine is being monitored to determine the Compton interference ratio, K, the same chlorine count can be used to correct for chlorine interference. In the particular case being considered, the chlorine concentration could vary by ± 30%. The percentage effect this would have on net hafnium counts is shown in Fig. 8. Correcting for both these variables resulted in the hafnium values shown in Fig. 9. These data were obtained from a number of runs with hafnium concentrations varying from 0.38 to 23.8 ppM on a solution basis. With all major corrections, the hafnium

concentration can now be expressed by the following equation:

$$\text{Hf in ppM} = ZG\,(T - B - K_0 Y)/\exp(-\lambda t) \quad (3)$$

where K_0 is the ratio K adjusted for specific-gravity changes and Z is a correction factor that accounts for the flux depression due to chlorine.

With this equation and the corrections described above, the hafnium can be measured between 0.5 and 30 ppM with ± 10% accuracy, assuming the flow rate is controlled to ± 1%. In assessing the accuracy of these results, we considered counting statistics as well as systematic and electronics errors.

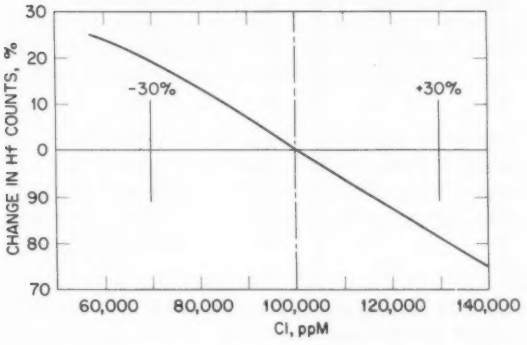

Fig. 8 Percentage change of net Hf counts with Cl concentration.

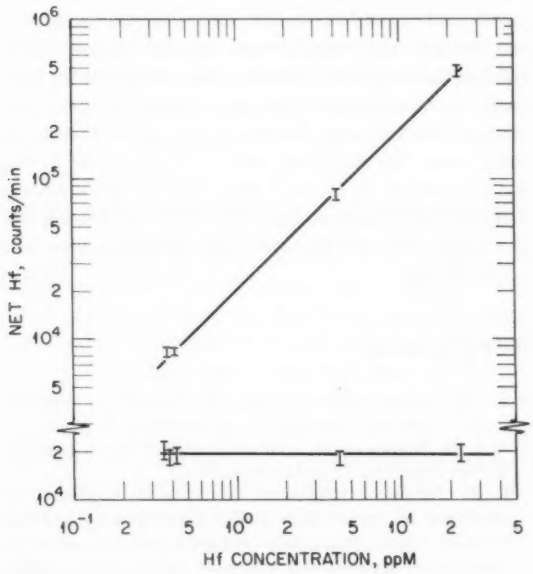

Fig. 9 Corrected values of net Hf counts vs. Hf concentrations.

Under the same basic approach, aluminum at a concentration of 28% in a sodium nitrate solution was determined with an accuracy of ± 1%. This very high concentration of aluminum determined meant that the ^{124}Sb sources did not have to be changed more often than every 12 to 18 months.

The SHERLOCK prototype system was also tested with a solution of copper, molybdenum, and aluminum as a check on the feasibility of determining copper and molybdenum on-stream. Aluminum is considered to be the interfering element, with copper and molybdenum being the elements of interest. The main peaks identified for molybdenum are at 0.193, 0.31, and 2.03 MeV. The copper peaks are at 0.511 and 1.04 MeV, and the aluminum peak is at 1.78 MeV. In this case, there is an interference in the copper region from both aluminum and molybdenum. The use of the 2.03-MeV peak for molybdenum eliminates the interference from aluminum or copper. At a flow rate of 1 gal/min, a 10-min delay time, and a 10-min counting time, copper can be monitored at the 0.35% level and molybdenum at the 0.05% level in the presence of 1% aluminum. In this case, the counting statistics would be approximately ± 1% for copper and ± 4.4% for molybdenum. Total analysis time for these measurements would be 25 to 30 min.

In a second circuit with molybdenum as the main element at 0.12% and copper present at 0.001%, with the aluminum still present at 1%, the molybdenum can be measured with counting statistics of ± 2.8%. The low copper concentration combined with aluminum makes accurate monitoring of the copper at this level rather difficult. However, by using longer delays or more elaborate counting equipment, the copper can be measured in this circuit.

A potential trouble spot in a Cu–Mo circuit would be the presence of uranium in the sample. Irradiated uranium gives molybdenum as a fission product, which would contribute to the molybdenum peak. The exact magnitude of this interference has not yet been measured; however, any circuit measuring molybdenum should be checked for uranium.

A number of other single elements have been tried in the SHERLOCK program to check calculations and set maximum sensitivities at which the elements can be determined (Table 1). Because of the many possible combinations of elements, potential applications should be tried experimentally to establish feasibility. Units are available at AECL in Ottawa and at B.C. Research in Vancouver for this purpose.

Table 1 Sensitivities for SHERLOCK*

Element	ppM†	Element	ppM†	Element	ppM†	Element	ppM†
Al	1.2‡	F	74	Mo	250	Ag	0.8
Sb	35	Gd	6.4	Nd	23	Na	53‡
Ar	6.5	Ga	25	Ne	92	Sr	57
As	45	Ge	12	Ni	1,650	S	10,000
Ba	70	Au	3.2	Nb	300	Ta	45
Be	ND	Hf	0.085‡	N	ND	Te	30
Bi	ND	He	ND	Os	5,500	Tb	450
B	ND	Ho	30	O	ND	Tl	ND
Br	4	H	ND	Pd	18	Th	30
Cd	190	In	0.04	P	ND	Tm	ND
Ca	190	I	1.5	Pt	70	Sn	95
C	ND	Ir	11	K	1,700	Ti	20
Ce	2,100	Fe	ND	Pr	300	W	68
Cs	25	Kr	210	Re	36	U	1.7
Cl	90‡	La	32	Rh	0.1	V	0.1
Cr	12,000	Pb	ND	Rb	190	Xe	140
Co	1.5‡	Li	ND	Ru	480	Yb	55
Cu	2‡	Lu	8.7	Sm	1.7	Y	7,200
Dy	0.11	Mg	62‡	Sc	0.037	Zn	1,200
Er	20	Mn	0.5	Se	0.8	Zr	56,000
Eu	0.4	Hg	1,300	Si	ND		

*Assuming no major interferences, a flow of 1 gal/min (imperial), counting accuracy of ± 5%, two 5- by 4-in. NaI detectors, analysis time ≃ 6 min, and a source strength of 3900 rhm.

†ND means not detectable assuming a cutoff level of 310 counts/min. (Fe, S, Si, and Cr should have better sensitivities with the fast-neutron model.)

‡Verified experimentally (June 1969).

ADVANTAGES AND DISADVANTAGES OF THE NAA SYSTEM

On recapitulation of the discussion of NAA systems, some great advantages become apparent. Sampling of a fairly large volume of material eliminates the possibility of small fluctuations giving erroneous results. The basic irradiation and counting system is relatively simple and has few moving parts to cause maintenance problems. The irradiation part of the unit is self-powered and is not susceptible to power failures or fluctuations. The highly penetrating nature of the neutrons and the high energy of the resultant gamma rays make fluctuations in density and particle size less critical than they are in X-ray-fluorescence systems. Exact measurements of these variables are now being made by B.C. Research. Another benefit is the elimination of the thin windows that are required for X-ray fluorescence but not for NAA.

The main disadvantage of any system using NAA is the possible interferences from other elements in the stream. Although a number of common elements like iron and silicon are not activated appreciably, certain other common elements like aluminum and manganese can severely limit sensitivities. Another feature of the NAA technique which can be a disadvantage is the time taken to complete an analysis, although in many mill applications this time factor may not prove critical. In most cases, the minimum analysis time will be 5 min, with an average of 10 to 15 min. One to three elements can usually be done in this time. Some techniques, like the copper and molybdenum determinations, may take up to 30 min. (RHL)

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Recent DID Radiometric-Technique Developments

By Martha Gerrard

Supplementary Keywords: *tracer; industry, utility; industry, transportation; flow measurement; military; measurement, density; measurement, other; forensics; activation analysis;* ^{82}Br; ^{85}Kr; ^{137}Cs.

Abstract: *The status of several DID radiometric-technique projects is reviewed: a nuclear helicopter lift indicator (NUHELI) (*^{85}Kr*), an isotopic shock-wave-position sensor (*^{85}Kr*), tracer measurements of turbine and pump discharge (*^{82}Br*), an airborne system for measuring the snow cover (*^{137}Cs*), and application of activation analysis to identification of paper and bullets and detection of gunpowder.*

For a number of years the USAEC's Division of Isotopes Development (DID) has encouraged, through contracts to commercial firms and research groups, the development of instruments and techniques using radioisotopes.

A number of gages and techniques on which the development work is rather far advanced have been described earlier in *Isotopes and Radiation Technology*,* e.g., gages for determining (*a*) the level of propellant in a tank, (*b*) eggshell strength, (*c*) stream current velocity (DWICA), (*d*) methane, (*e*) suspended-sediment concentration, (*f*) bottom-sediment density, (*g*) the presence of life on other planets (Gulliver), (*h*) the water equivalent of a snow cover, and (*i*) ore components. Several gages and techniques related to pollution control, including sand tracing, are described in *Isotopes and Radiation Technology*, 8(4).

NUCLEAR HELICOPTER LIFT INDICATOR

Knowledge of the lift potential of a helicopter, or lift margin if the vehicle gross weight is known, is even more necessary than for fixed-wing aircraft because helicopters experience a considerable ground effect, i.e., a lift enhancement within one rotor diameter of the ground (40 to 60 ft for contemporary machines). Thus, the machine may have moved away from an adequate landing site, or, in the case of military machines, may have entered enemy-fire range, before it becomes evident that the lifting power is less than the gross weight. Since the maximum lift potential of the rotor depends on the ambient-air density and since the available engine torque is a function of the air temperature, a very useful device would be one that could measure the air density and temperature and from the data compute the maximum available lift. Ideally, the device would operate while the vehicle is on the ground (rotors turning or stopped), hovering, or cruising.

General Nucleonics Division of Tyco Laboratories Inc. (Pomona, Calif.) has demonstrated[1] the feasibility of a lift-indicator system—the NUHELI (Fig. 1)—that uses a density sensor based on ^{85}Kr bremsstrahlung backscatter to measure air density and a thermistor to measure air temperature. From the data, the maximum helicopter lift potential is calculated with a computer. The proposed mounting of the sensors on the helicopter body is shown in Fig. 2.

A model of the system was tested in altitude, temperature, and humidity chambers and on the Palm Springs, Calif., funicular railway, which runs from an altitude of 2650 ft to 8500 ft. These tests demonstrated the ability of the system to measure air density at levels from 0 to 12 thousand ft to ±0.5% and air temperature from −40 to +60°C to ±0.93% (±275 lb in a 30 thousand-lb gross-weight helicopter) (Fig. 3). The humidity test showed that air moisture up to 100% relative humidity at 110°F affected the indicated lift readout <1%. Although not included in the model, the starting gross weight of the helicopter plus fuel could be input to a momentary gross-weight computer. A digital comparator could then read out "lift margin," and "go" and "no-go" lights would indicate to the pilot whether conditions were safe for landing or takeoff.

Density Sensor

The density of the outside air is measured, through the helicopter skin, by determining the amount of bremsstrahlung from an inside source which is backscattered from the outside air. The radiation source is ^{85}Kr gas sealed in a 0.030-in.-wall copper capsule lined with 0.002 in. of depleted uranium. Bremsstrahlung is produced when the ^{85}Kr beta radiation is stopped in the uranium, and the emission is controlled by a rotating shutter (collimator) (Fig. 4). When the shutter

*See, for example (*a*) **5:** 286-287; (*b*) **5:** 284-286; (*c*) **5:** 208-212; (*d*) **6:** 368-375; (*e*) **4:** 358-362; (*f*) **3:** 216; (*g*) **4:** 108-110; (*h*) **4:** 231-237; (*i*) **5:**280-284.

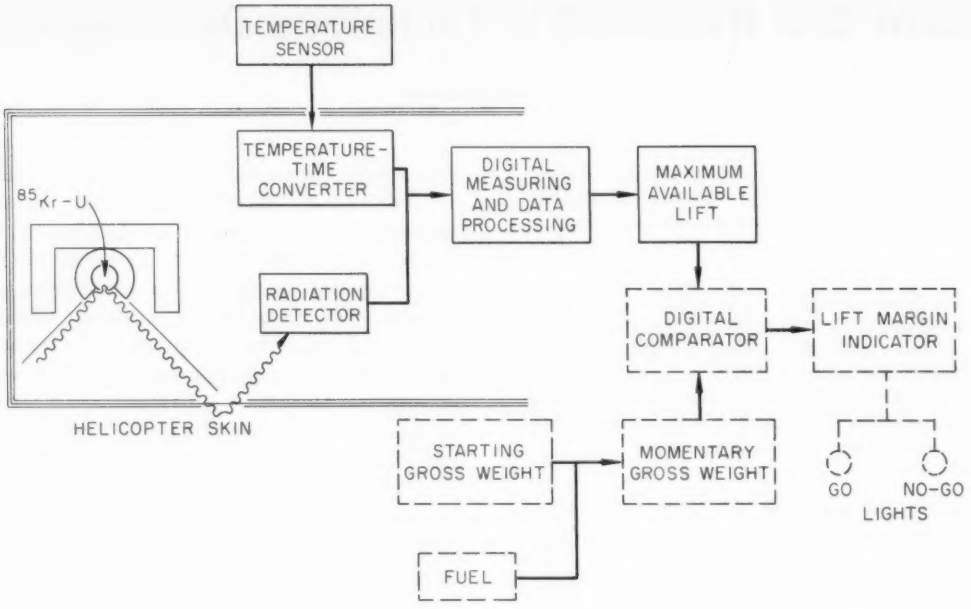


Fig. 1 Basic NUHELI system elements. The dotted-in blocks indicate units that could be added but were not in original system.

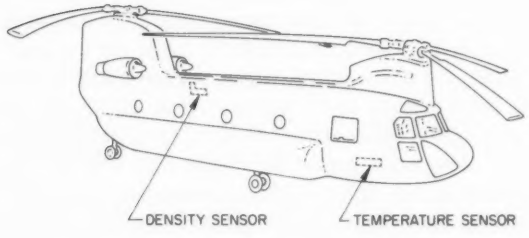


Fig. 2 Proposed location of the density and temperature sensors on the helicopter. The density sensor is mounted inside the helicopter skin and the temperature sensor outside, underneath the fuselage.

is open, the bremsstrahlung is backscattered from the outside air into a NaI scintillation detector, and the counts are added for about 5 sec, the time being determined from the air temperature by means of a frequency (time) output from the temperature sensor. Then the collimator rotates to the closed position, aligning a small hole in rotating and stationary collimators from the source through to the crystal, and the sensor accumulates counts in the calibration mode. Actually, the counts from the first cycle are counted out of a register, and the time to empty the register is displayed as lift potential. The total cycle time is 8 to 10 sec.

The detector for the backscattered bremsstrahlung must have good efficiency, be capable of recording fairly high counting rates, and operate over a temperature range of −54 to +71°C with 0.2% count-rate stability. A 2-in.-diameter by 1-in.-thick NaI scintillator unit was selected, and its temperature instability was compensated by an automatic gain control system containing a 0.5-μCi ^{137}Cs source. This radionuclide emits a 662-keV ^{85}Kr gamma. The scintillator is coupled to a magnetically shielded photomultiplier tube.

Temperature Sensor

The temperature sensor (Fig. 5) is a thermistor with a small volume and consequently small thermal lag. It is mounted on the lower part of the helicopter body to avoid radiant heating from the sun and is thermally insulated from the helicopter. It protrudes ~0.25 in. into the air.

ISOTOPIC SHOCK-WAVE-POSITION SENSOR

Knowledge of the position in the throat region of the normal shock wave—a flow discontinuity in-

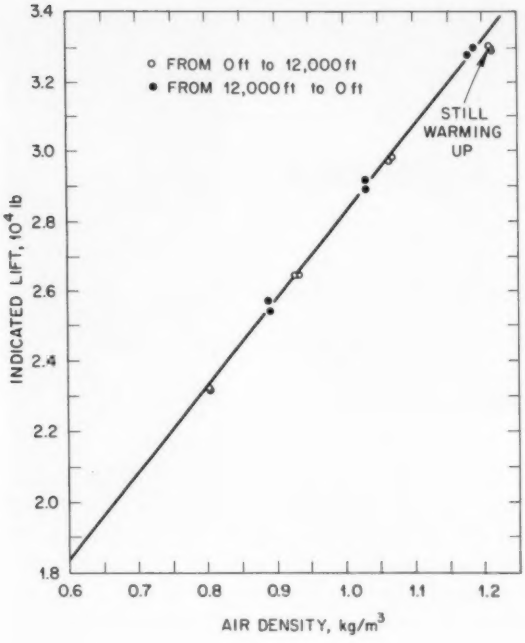


Fig. 3 Results of a test on a model of the NUHELI system in a Langley altitude chamber.

volving a change from supersonic to subsonic flow speed with a subsequent pressure rise—is necessary to maximize the efficiency of a mixed compression supersonic inlet system. Lambda-shock-wave and boundary-layer effects may cause inaccuracies in the commonly used pressure-profile-measurement methods, and a system that is less subject to these inaccuracies and has a faster response was needed. The feasibility of a radioisotopic system developed by Industrial Nucleonics Corporation (Columbus, Ohio) was demonstrated[2] following a study made for Wright–Patterson Air Force Base which had indicated that shock-wave position can be measured by a radioisotopic technique.

The radioisotopic shock-wave-position sensor consists of three 10-Ci ^{85}Kr sources with three ionization-chamber radiation detectors plus three electrometer amplifiers and associated electronics (Fig. 6). The position of the shock wave is determined from upstream, downstream, and transverse air-density values, which are measured by the attenuation of the ^{85}Kr beta radiation as it passes through the air. The transverse measurement provides the shock-wave-position information, with compensation for ambient conditions and Mach-number variations being provided by the upstream and downstream measurements.

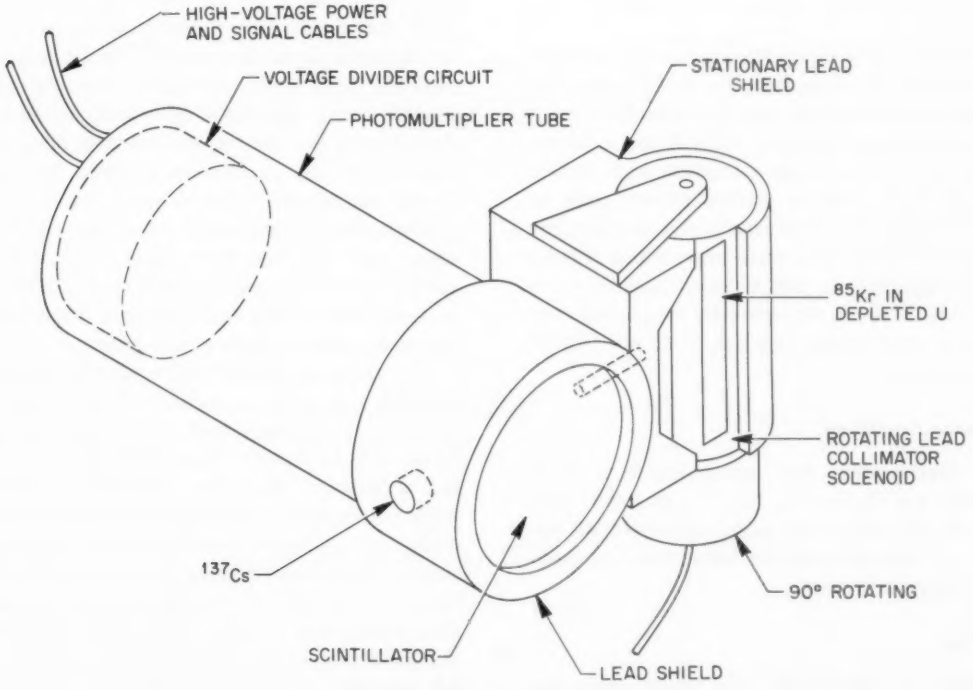


Fig. 4 NUHELI density sensor.

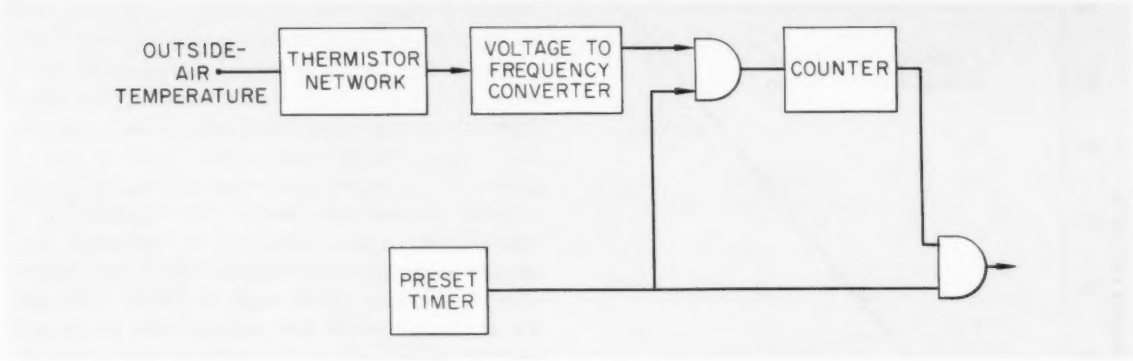


Fig. 5 Temperature-sensor design.

Sources

The 10-Ci ^{85}Kr sources, fabricated by American Atomics of Tucson, Ariz., were encapsulated in titanium to minimize bremsstrahlung production. Each source was a 0.625-in.-inside-diameter tube, 0.750 in. in outside diameter, with a total length of 1.75 in. and an active length of 150 in. A 0.002-in. titanium window was welded to the tube. The tube was filled with krypton (enriched to 25% in ^{85}Kr) at 4 atm pressure.

Detector

The detector is a xenon-filled ionization chamber, 1 in. in diameter by 1¾ in. long. The shell is brass, with a 0.25-mil stainless-steel window. The ionization chamber had a statistical efficiency of 80% and a current efficiency of ~37%. Voltage-saturation tests showed that a significant drift in applied voltage could be tolerated without noticeable error in the measurement. Response was found to be much faster with a negative applied voltage, 400 to 500 V being satisfactory. A range of ±10°F about the operating temperature was necessary to limit voltage variation to <1 mV (<0.1% of output voltage).

Electrometer Amplifiers

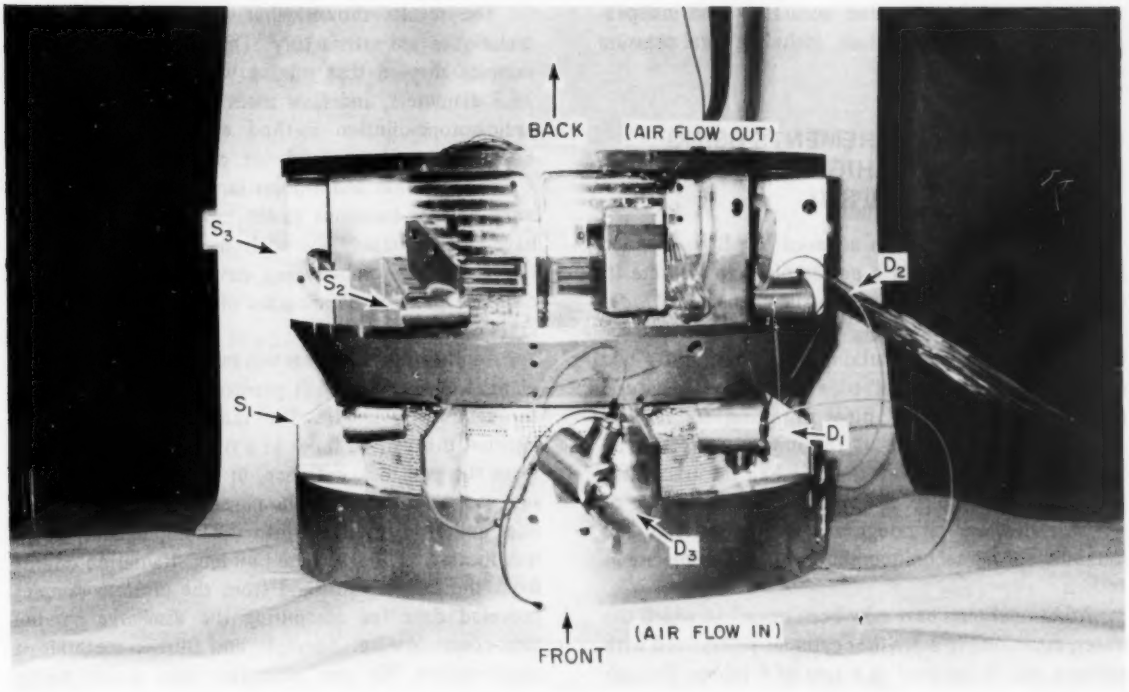
The electrometers were assembled in a metal housing that was 3¼ by 1 15/16 by 1 15/16 in. Power from the rack supply, which was quite stable (±15 V), was supplied to each through its own cable to avoid crosstalk and ground loops.

System Tests

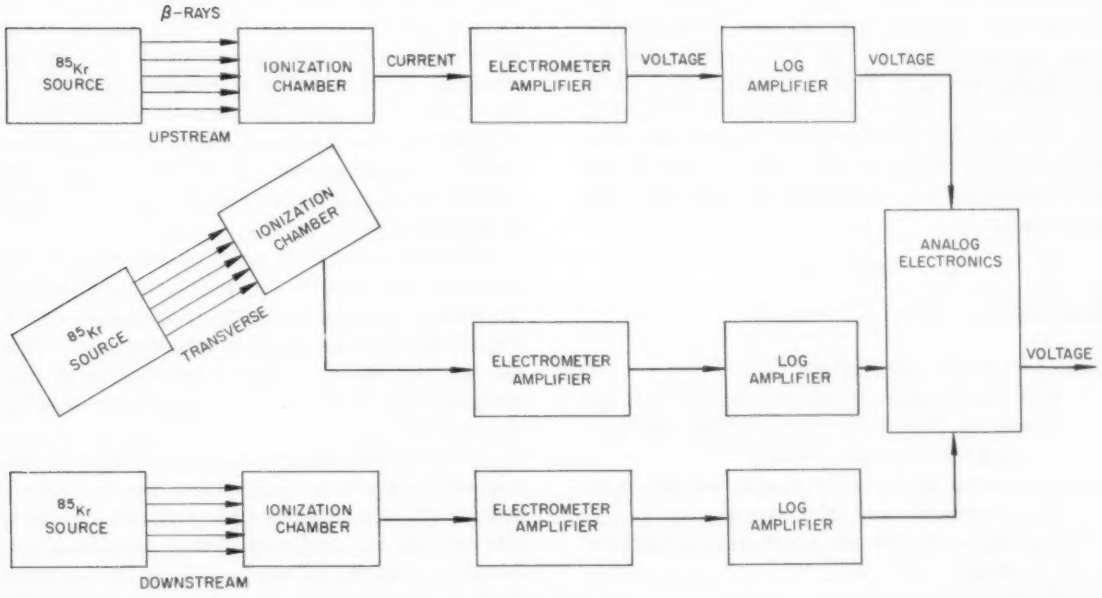
A model of the system was tested inside the Mach 2.65 axisymmetric inlet system, which was mounted in the 8- by 7-ft wind tunnel at Moffett Field, Calif. The unit was installed in the outer cowl body of the inlet. Useful data could not be obtained with the instrument when it was statically calibrated, and a dynamic calibration was carried out by running the tunnel at Mach 2.65 and several different total pressures.

For the first test, the upstream and downstream sources were removed to eliminate crosstalk so as to be able to examine the sensitivity of the transverse signal. Tests were made at 30, 25, and 20 in. Hg total pressure with the shock wave initially downstream of the aerodynamic throat but moved forward in increments until the shock wave was expelled from the throat, its position being determined after each movement. The data showed that the transverse density signal was very sensitive to the shock-wave position and that the system can measure shock-wave instabilities unseen by systems using static-pressure measurements. However, when only the transverse measurement is used, the system must be zeroed and calibrated for each change in total pressure and Mach number. Therefore a test was made using the three-source system.

To eliminate crosstalk when all three sources were installed, lead wool was packed around the sources and detectors to attenuate transverse bremsstrahlung. The signals due to forward bremsstrahlung were measured and subtracted from the appropriate electrometer signals. A dynamic calibration of the system was again made, and all three source–detector units were installed. Shock-wave-position determinations made at Mach 1.75 to 2.5 with the three-source system were then satisfactory. Certain calibration deficiencies in this preliminary work prevented demonstration of the full capability of the system. However, all indications were that, with suitable static calibration, shock-wave



(a)



(b)

Fig. 6 (*a*) Cowl section of radioisotopic shock-wave-position sensor and amplifiers and (*b*) block diagram.

position could be measured accurately and independently of all flow conditions, including total pressure and Mach number.

DISCHARGE MEASUREMENTS USING RADIOISOTOPES IN HIGH-HEAD TURBINES AND PUMPS. II

A technique in which aqueous $K^{82}Br$ is injected into the discharge from a power plant to measure its rate of flow, described in an earlier issue of *Isotopes and Radiation Technology*,[3] was developed by the U. S. Bureau of Reclamation. The earlier tests had indicated the lengths of pipe required for natural turbulence to mix the pipe flow and tracer. For example, a mixing length of 164 pipe diameters, in an 8-ft-diameter pipe, was sufficient when the tracer was injected near the pipe sidewall into water flowing at 6 ft/sec. However, although the results indicated the suitability of the technique, they were not so precise as desired.

Additional tests have now been made[4] in which the tracer, contained in a 3.7-liter cylinder pressurized with nitrogen gas, is injected at a rate of 8 ml/sec through four 0.25-in.-diameter stainless-steel tubes, restricted by $\frac{1}{64}$-in. orifices, which project 8 in. (~0.2 of the pipe radius) into the flow. The tracer was injected at four points, 90° apart in the circumference of the 7-ft-diameter penstock. Samples were taken from the same angular locations in the pipe at 36.5 diameters downstream and again from a single 0.25-in.-diameter hole at 919 diameters, at the entrance to the turbine (Fig. 7). The radioactivity in the samples was determined by counting at the site, using a mobile laboratory. Discharges were calculated from the basic dilution equation,

$$Q = qC_1/C_2 = qC_1fF/R_n$$

from which $C_2 = R_n/fF$ or $F = R_k/C_s$,

where q = injection rate (ml/sec)
C_1 = concentration of injected solution (μCi/ml)
f = decay correction factor (variable with time and therefore not constant)
F = calibration factor for sample flask and shield
C_s = concentration of calibration solution
$R_n = (R_g - R_b)/f$ = net count rate corrected for decay
R_g = gross count rate
R_b = background count rate
R_k = net count rate from calibration solution corrected for decay

The results showed that sampling and counting techniques are satisfactory. The data from individual samples showed that mixing was not satisfactory at 36.5 diameters, and flow measurements made by the radioisotope-dilution method were lower than flowmeter values determined for comparison. Both the 4-point injection and 4-point sampling occurred in the same angular locations in the pipeline. If these could have been rotated 90° with respect to each other, larger discharge values may have been indicated because of possible deficiencies of tracer in these quadrants of the pipe.

Another series of tests was made at Pole Hill power plant, where the 2044-ft penstock is 8 ft in diameter throughout its length. The radioisotopic tracer was injected through 40 holes in a ring manifold upstream from the penstock entrance, in the gate structure. A sample was taken from the penstock near the turbine inlet and from the flow into the sample tank, which was located in the turbine building. Radiation counts from the sample tank and from the discrete samples provided data for computing the discharge by the total-count, integrated-sample, and dilution methods of measurement. No one procedure was shown to be superior to the others.

Although the radioisotopic method was shown to be satisfactory, minor improvements in procedures may still be necessary. Differences in flow rate indicated by the three isotope computation methods may be reduced by further refinement of sampling and counting techniques. These measurements indicate that, with 255 pipe diameters of mixing length, multiple injection points, and a stable counting system, discharge measurements can be made with radioisotopes to an accuracy within an estimated probable 2σ error of 1.5%.

The time required to make measurements is long compared with that for the salt-velocity and pressure-momentum methods, but the time required for installation of injection and sampling equipment is less than for the salt-velocity method. Automation of both methods might lessen the time factor in favor of the radioisotopic.

The methods and procedures developed in the program for discharge measurement may be used for closed and in some cases open conduits—wherever radioisotopes are applicable. Exact procedures that should be carefully followed to obtain the maximum accuracy and precision have been described.[5] The method is considered to be a technique of measurement for intermittent use and not for continuous-discharge measurement.

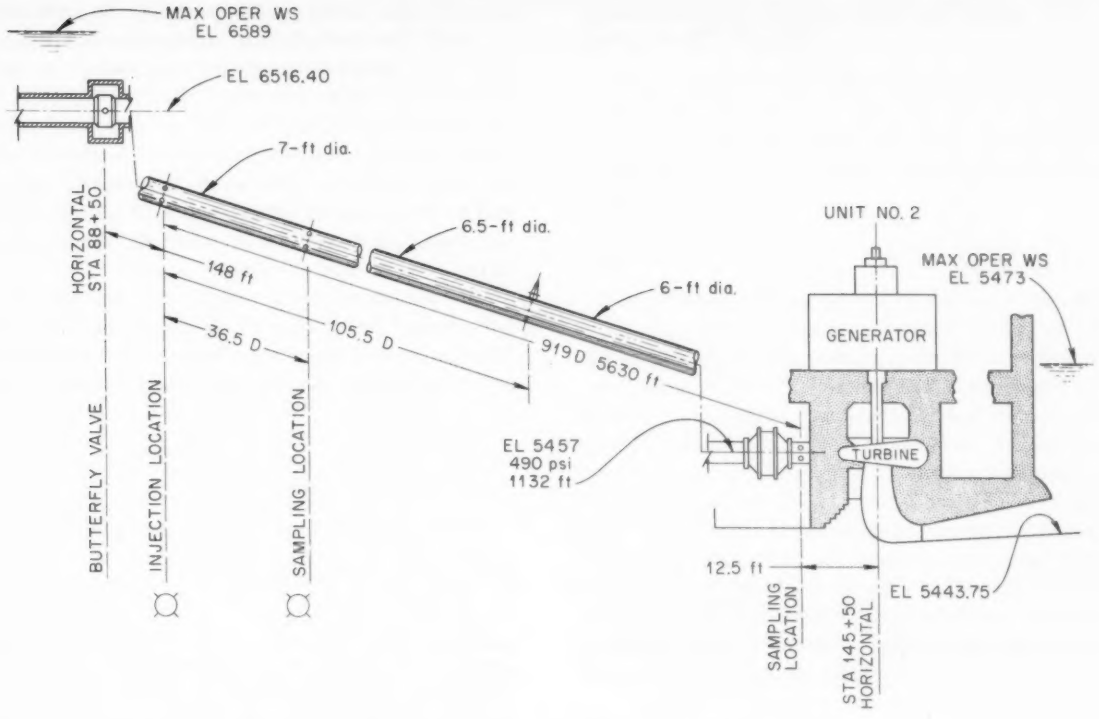


Fig. 7 Injection and sampling locations in Flatiron Power and Pumping Plant penstock section.

AIRBORNE RADIOMETRIC SNOW-SURVEY SYSTEM

The value of making late-winter snow surveys is well established. Unfortunately, methods now in use require either actual visits to each data-collection point or permanent instrumentation at each point as well as at a remote receiving station. Both procedures are costly even when feasible.

An airborne radiometric snow-survey system has been developed[6] at Montana State University, under contract to the Division of Isotopes Development and the Bonneville Power Administration, which eliminates all in-situ instrumentation. The technique is merely an extension of one in common use—the gamma radiation from a ground-level source, after being attenuated by the snow cover through which it passes, is detected from an airplane by airborne instrumentation. Preliminary tests with a prototype system demonstrated its feasibility.

The airborne radiometric snow-survey system is based on the principle that gamma radiation is absorbed by water molecules as it passes through a layer of water—or, in this case, snow. If a gamma-emitting radioisotope is placed at ground level and the count rate noted at a specific altitude before any snow falls, the count rate determined at the same altitude after snow has fallen can be converted to water equivalent of the snow pack. The relation is

$$I = I_o b e^{-\mu d}$$

where I = measured gamma flux
I_o = original gamma flux
b = dose-buildup factor
μ = linear attenuation coefficient
d = attenuator (i.e., snow) thickness

This ideal relation can, of course, be only approximated in practice.

The system (Fig. 8) is very simple in theory. A radioisotope, in its lead-shielded shipping cask, is located just below ground level. A collimator, or a narrowed neck in the shipping cask, directs the radiation upward in a narrow cone, and, as the beam passes through the snow cover, some of the radiation is

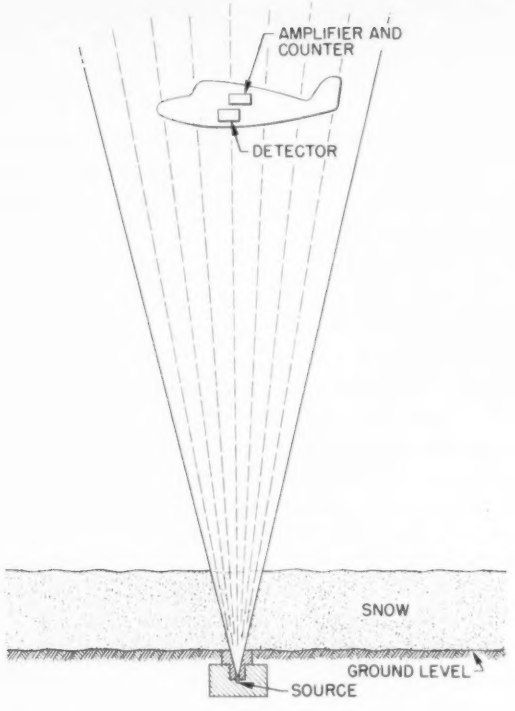


Fig. 8 Radiometric airborne snow-survey system.

absorbed. The radiation that passes through is measured by instruments in a plane that flies over the area when a measurement is to be made. A ^{137}Cs source with an activity of about 2.6 Ci was used in the prototype system.

The source shipping cask is installed on a concrete pad at the bottom of a shallow pit. The fence surrounding the source-installation plot is of nonclimbable wire and at least 6 ft higher than the maximum expected snow depth for the area. Barbed wire at the top is a further deterrent to entry of the enclosure. Radiation warning signs are posted.

System Tests

Eleven test flights, following four calibration flights, were completed. After the source had been installed in Gallatin National Forest, Mont., on Feb. 12, 1970, a zero-water value was determined. Then, by means of a blower, the source was covered with snow to the level of the surrounding snowpack. This snow cover was somewhat denser than that in other areas, as shown by the difference between the flight data and data from a nearby pressure pillow. On May 13, when the snow-water content was maximum (21.8 in ± 4 to 5 ft of snow), radiation levels were very low. The differential between the water content of the denser snow over the source and the snow in surrounding areas was ~4.3 in., as shown by gravimetric samples taken by a ground crew. Some differential was maintained throughout the season, with a gradual trend toward consistency. A zero-water count was made again on June 10, when all the snow had melted.

Snow-water-equivalent values were measured by a 6-ft pressure pillow (Fig. 9) for comparison with the data determined from the airborne counting instruments. Snow-tube samples were taken in some of the

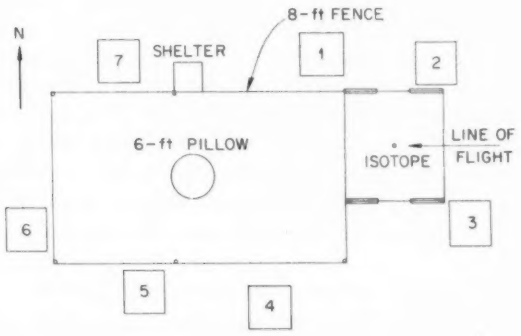


Fig. 9 Arrangement of radioactive source and other snow gaging installations for comparison of results. Numbers 1 to 7 are snow-tube sampling sites.

ground trips, but no data were available for comparison with the radiometric. Allowing for the difference in density of the snow cover blown over the source, after the first zero-water reading the agreement between the radiometrically determined values and those determined by standard methods was generally good (Table 1). Errors due to differences in aircraft altitude and path, isotope decay, and other variables must, of course, be considered in calculating the results.

Advantages and Disadvantages of Radiometric System

Cost comparisons are difficult because snow-survey systems are often tailored to a particular situation. However, a preliminary estimate indicates a slight advantage for the airborne radiometric system over systems requiring ground visitation. (Details are given in the report.) A significant advantage of the airborne system is a reduction in field staff, which also decreases

Table 1 Comparison of Snow-Water Equivalent Determined by Radiometric Method with That Determined by Other Methods

Date 1970	Snow-water equivalent, in. ^{137}Cs	6-ft pillow	Difference
Feb. 12	0.5	8.1	
Source Covered with Snow			
Feb. 20	14.6	9.4	5.2
Mar. 5	14.9	9.4	5.5
Mar. 11	15.8	10.1	5.7
Mar. 20	17.1	12.7	4.4
Apr. 9	19.1	16.0	3.1
May 4	22.4	19.6	2.8
May 15	20.2	17.1	3.1
June 3	6.9	0.0	
June 5	4.6	0.0	
June 10	0.7	0.0	

training costs, over-snow machines, and sampling equipment when used as a backup system for systems now in use. It may replace other systems in isolated areas. With the radioactive system, early- and late-season surveys can be made when trucks cannot transport over-snow machines to the snow line. Travel of small over-snow machines on sampling sites is eliminated, and courses can be better located when access by over-snow travel is not a consideration. Annual maintenance cost is low. Its accuracy at depths significant for forecasting has been demonstrated to be equivalent to that obtained by pressure-pillow sensing and is better than that of the gravimetric-sample technique. Certain expected innovations promise to improve accuracy at very shallow water depths by increasing the slope of the attenuation curve at this point.

Disadvantages are the initial cost and the limitation to one-point sampling, which is not serious if the point is properly located.

It appears that 30 in. of water equivalent is a practical limit for ^{137}Cs. The cask required (approximately 200 lb) is transportable without mechanical assistance. Beyond this depth, to approximately 50 in. water, ^{60}Co will be necessary, and the resulting cask weight will require helicopter installation or accessibility of site at least in summer to ground transportation. Forty-eight to 50 in. water may be the practical limit to the system regardless of type of source. Tests with ^{60}Co are planned for the future.

FORENSIC NEUTRON ACTIVATION ANALYSIS

Three reports[7-9] have been issued recently by Gulf General Atomic Inc. on forensic use of neutron activation techniques: (1) for identifying paper, (2) for identifying bullets, and (3) for detecting gunpowder residues.*

Paper

Results were encouraging in the efforts to identify paper by neutron activation determination of its elemental composition. Weighed samples were reactor activated at ~2×10^{12} thermal n/(cm^2)(sec), and the induced radioisotopes were identified and the amounts present determined. Five elements—Ti, Al, Ca, Na, and Mn—varied 35% or less for different samples of the same paper, while Cl, Cr, and Sb varied 41, 70, and 68%, respectively. Although these concentrations differed by several orders of magnitude, the much greater variations from one kind of paper to the next resulted in highly distinctive elemental "fingerprints." Only two papers—both 25% rag paper from the same manufacturer—had the same fingerprints.

Inasmuch as only antimony appeared to have a Gaussian concentration density among the various kinds of paper, the individual pragmatic densities were tested for independence and statistical applicability. Expected observation frequencies of all possible concentration pairs between aluminum and the other elements were hypothesized to be no different than the observed pair frequencies. The hypothesis was not rejected by the chi-square test. Hence, there is a basis for calculating the probability of observing a particular fingerprint in paper. This is of particular importance in estimating the chance that two specimens of paper with the same element fingerprint as, say, an evidence sample and a suspect sample, might actually be different papers. The findings indicate that the chance of thus mismatching papers is small, but a larger data base is needed to more fully develop the statistics of the population of papers.

The possibility of detecting ink on paper by a neutron activation technique was not encouraging.

Bullet Lead

The use of concentrations of Sb, Cu, and As, as determined by neutron activation analysis, for identi-

*See *Isotopes and Radiation Technology*, 4: 325-340 for an earlier discussion of this field.

fying bullets does not appear promising. Bullet-lead samples taken from 75 different lots of bullets were reactor activated in a flux of $\sim 2 \times 10^{12}$ thermal n/(cm^2)(sec), and the induced radioactive Sb, Cu, and As were measured by multichannel gamma-ray spectrometry. Intralot uniformity of bullet leads with respect to the three elements was good with relative standard deviations of ±4% for antimony, ±23% for copper, and ±44% for arsenic. Appropriately, antimony is the most useful element for comparison purposes. Also, copper and arsenic concentrations correlated with antimony concentrations.

Unfortunate for the forensic utility of the technique was the frequency with which antimony concentrations were in the range 0.7 to 0.8%. This factor, coupled with the correlated concentrations of copper and arsenic and the larger variances of these two elements, contributed in large measure to the finding that less than half of the 75 lots of bullets were uniquely characterized by the concentrations of Sb, Cu, and As. Thus, although a significant difference in concentration of any one of the three elements indicates that two bullets came from different lots, matching concentrations of all three elements does not indicate that two bullets come from the same lot.

Gunpowder Detection

The idea of use of neutron activation analysis to identify traces of Ba and Sb (from the cartridge primer) in residue material removed from the back of the gun hand, and thus determine whether a person has recently fired a handgun, has been under study for a decade.

During the last 2 years of the investigation, large-scale statistical studies were conducted on gunshot residues from revolvers and automatic pistols of various common calibers and of Ba and Sb present on the hands of persons, of various occupations, who had not recently fired a gun. Statistical treatment of these data by the bivariate-normal (BVN) method—actually a bivariate log-normal treatment developed for this purpose—has indicated that, in most instances, properly obtained and properly interpreted Ba–Sb results can provide a fairly definitive distinction between a hand that has recently fired a handgun and one that has not—or one that has subsequently been washed clean before being examined.

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Atomics International's L-88 Nuclear Reactor for Neutron Radiography

By J. O. Henrie*

Abstract: *The nuclear reactor fabricated by Atomics International for neutron radiography is described.*

The L-88 reactor is designed expressly for neutron radiography. The reactor core provides a maximum ratio of collimated-neutron-beam strength to reactor thermal power. The low thermal-power requirements result in system simplicity and compactness, which in turn hold the initial costs and subsequent operating and maintenance costs to a minimum and allow the use of a sealed reactor system, since no refueling is required in its lifetime of 20 years or more. The complete reactor system is shipped in three preassembled packages (reactor, console, and cooler) designed for rapid, minimum-effort installation. The reactor can be moved to a new location with comparatively little difficulty.

The L-88 reactor can be provided with highly flexible experimental facilities for other nondestructive testing—e.g., activation analysis—as well as for research in physics, chemistry, and biology.

REACTOR DESCRIPTION

The characteristics of the L-88 reactor are summarized in Table 1. The reactor core is a 12.5-in.-diameter stainless-steel sphere (0.080-in.-thick wall) containing uranyl sulfate solution (90% enriched ^{235}U). Five cooling coils are required, each being made of 0.25-in.-diameter stainless-steel tubing 10 ft long. The stainless-steel fill-and-drain line is also 0.25 in. in diameter. Two cylindrical control and safety rods, containing neutron-absorbing material, are moved vertically through the sphere by two drive mechanisms. Beryllium followers provide extra control and decrease the neutron-flux depression in the core during operation. A neutron-beam tube, extending through the center of the core, contains a "flux trap" that can be filled with beryllium or other materials to enhance the neutron output. Filters and different materials in the trap shape the neutron beam and provide some control of the gamma-radiation intensity of the emerging beam.

Table 1 Characteristics of the L-88 Reactor

Design power level	10 kW
Neutron-beam collimation	Variable
Neutron-beam strength for resolution of L/d 100	1×10^7 thermal n/(cm²)(sec)
Average power density at 10 kW	1 kW/liter
Thermal flux at core center at 10 kW	5×10^{11} n/(cm²)(sec)
Fuel	Aqueous UO_2SO_4, 90% enriched in ^{235}U, critical mass 1 kg of ^{235}U
Coolant	Distilled natural water
Reflector	Graphite or beryllium graphite
Control rods (2 required)	Cadmium

The hydrogen and oxygen produced by radiolytic decomposition of the water in the fuel solution are recombined by a highly developed gas recombiner having no moving parts, which is included as an integral part of the reactor primary system. Inside the stainless-steel recombiner vessel is a catalyst consisting of ⅛-in.-diameter by ⅛-in.-long alumina pellets coated with platinum black.

Since the core and the recombiner system are hermetically sealed in their stainless-steel containers for the entire lifetime of the facility, no contaminants are released to the environment.

A console contains the instruments for monitoring and control of the reactor operation and operation of the radiograph shutters. An automatic controller can be included as a convenience in maintaining constant neutron intensity.

Because of the modest power level—10 kW—of the reactor, a refrigerated cooling system of 4 tons capacity adequately cools the reactor and releases the heat directly to the atmosphere.

The basic reactor assembly (Fig. 1), which includes a solid reflector and shutdown shield, is 32 in. in diameter by 74 in. high. This integral assembly is shipped to the building site and placed in an ordinary-concrete shield (Fig. 2).

*Atomics International Division, North American Rockwell Corp., P.O. Box 309, Canoga Park, Calif. 91304.

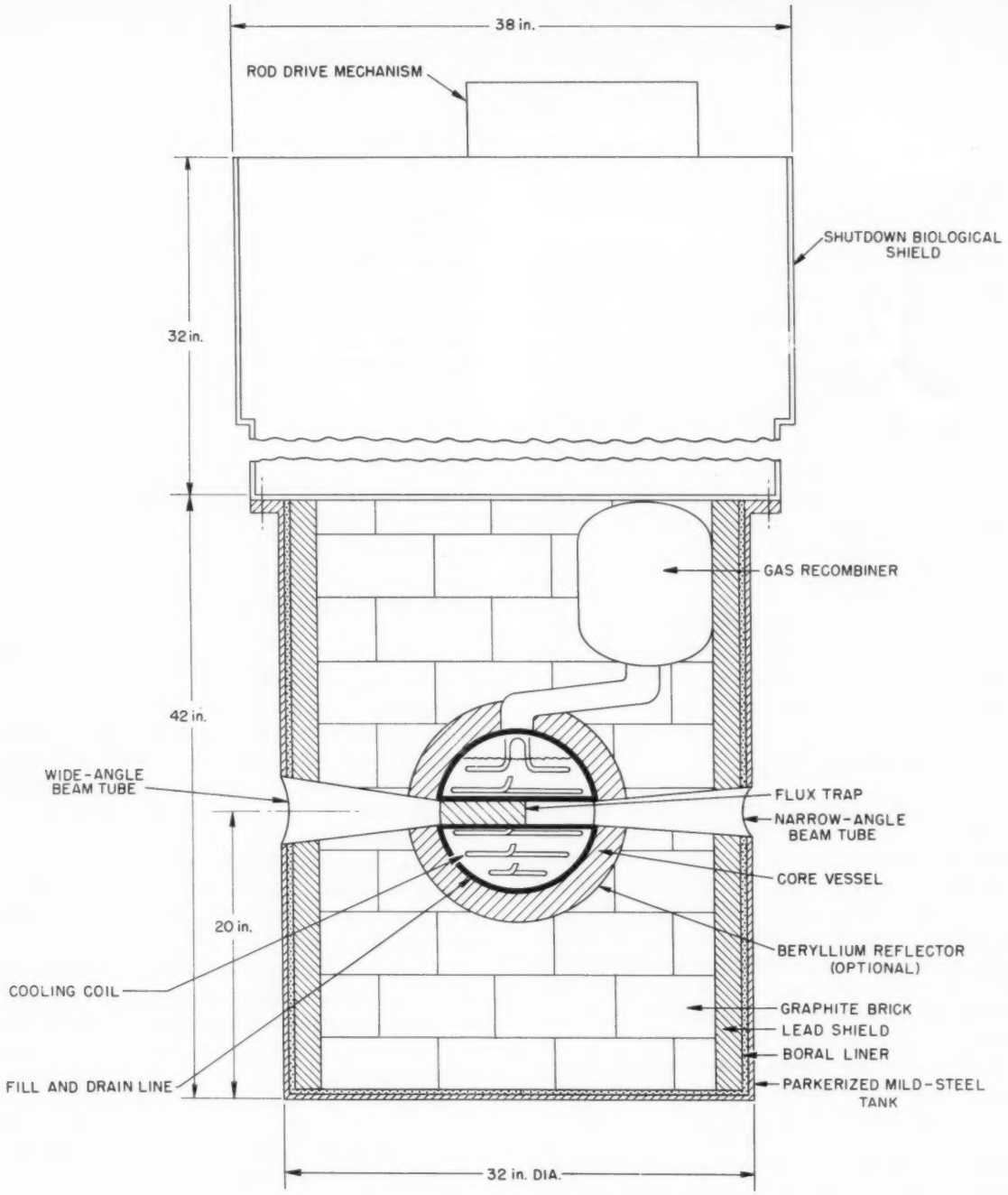

Fig. 1 L-88 reactor for neutron radiography.

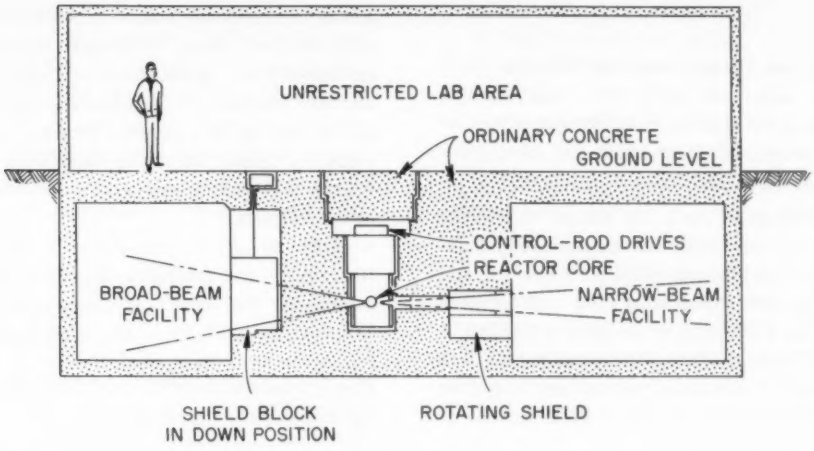

Fig. 2 One of many possible arrangements of the L-88 reactor system.

If desired, as, for example, in a hot cell where the object is in a fixed location, the assembly may be track-mounted in a shielded tunnel and moved away from or toward the target and image-detection area to vary the neutron optics.

NEUTRON-RADIOGRAPHY PARAMETERS

The L-88 reactor supplies neutrons of thermal, epithermal, and fast energies and can supply one vertical and as many as four horizontal neutron beams. The basic conical shape of these beams can be altered by changing the size and location of removable apertures.

An analysis of this particular reactor beam geometry and flux trap and measurements of thermal flux in the neutron beam of a similar reactor have led to a remarkably simple expression for Φ, the thermal-neutron flux in neutrons per square centimeter per second at the object being photographed,

$$\Phi = 10^7 P/R^2$$

where P is the reactor power in watts and R is the beam resolution, L/d, with L the distance from the aperture to the object and d the aperture diameter. This equation is valid (if air-scattering effects are ignored) for all points that project the full area of the aperture on the surface of the flux trap near the center of the core. With the reactor operating at 10 kW ($P = 10^4$) and with an object being radiographed 100 diameters from the aperture ($R^2 = 10^4$), the collimated thermal-neutron flux at the object is 10^7 n/(cm^2)(sec). Also, for a low L/d, e.g., around 25, the thermal-neutron flux at the object is 1.6×10^8 n/(cm^2)(sec), which is more than an order of magnitude higher than thermal-neutron fluxes currently available from nonreactor sources.

Safety

The L-88 reactor belongs to the family of homogeneous-solution reactors, which have a long history of reliability, sound technology, and safety and can be licensed for installation in virtually any area because of their excellent safety characteristics. They have a strong negative power coefficient of reactivity, which means that the reactivity decreases as the power level rises due to thermal expansion of the liquid fuel and formation of gas bubbles in it. A large power surge would expel fuel into a holdup area above the core and automatically shut the reactor down. This shutdown mechanism operates as a completely independent backup to the mechanical control and safety rods.

The reactor can be shut down in a fraction of a second by interrupting the current to the magnetic clutches that hold the control and safety rods, allowing them to fall by gravity. The interruption may be effected by a signal from any of the reactor safety devices or facility interlocks and ensures complete safety of the operation, analogous to the action of the interlocks of an X-ray system.

Costs

One person can operate and maintain the L-88 reactor and its associated equipment, and potential operators having good technical backgrounds require only 2 to 3 weeks of training to be adequately prepared for licensing by the AEC.

Neutron-radiography costs are related to (1) the time required for one cycle of neutron exposure, (2) the volume of parts radiographed per exposure, and (3) the time for film processing and radiographic interpretation. The L-88 reactor design is optimized to allow short cycle times and large arrays of parts (10 ft in diameter or larger) to be radiographed, and exposure times vary from a minute to an hour. Five minutes or less is normal, but longer exposures are required for very detailed image definition (slow film and high resolution) or penetration of objects having high neutron attenuation or scattering characteristics. Parts can be set up in a support area and then moved into place for radiography. The setup time depends on the volume and quality-assurance requirements for identification of parts.

Due to gross variations in the number, size, traceability, and resolution requirements of items being examined, the cost per radiograph varies widely. However, on a 14- by 17-in.-frame basis, total costs per frame can be, under ideal conditions, as low as $15. This estimate is based on our experience in radiographing more than 8 thousand parts. (MG)

A Radiometric Method for Sulfate Determination

By Edwin H. Klehr*

Supplementary Keywords: *material tracing; radiometric analysis; chemistry, analytical; water and waste treatment; pollution; comparison;* ^{133}Ba.

Abstract: *A radiometric method for the determination of sulfate in fresh water is described. The sulfate is precipitated with a barium chloride solution containing* ^{133}Ba, *and the resulting barium sulfate is filtered off and counted. The radioactivity of the supernatant liquid is also determined and can be used as a measure of the sulfate content. A comparison of the radiometric method to the standard gravimetric and turbidimetric methods showed that the precision and accuracy of all three methods were similar.*

Determination of the sulfate ion, one of the major anions present in natural waters, is important for several reasons, including the sulfate's potential cathartic effect, its tendency to form hard scales in boilers and heat exchangers, and its potential conversion to sulfide under anaerobic conditions.

The determination of sulfate has always been a problem for water analysts. Three basic methods are now used—gravimetric, turbidimetric, and volumetric procedures. Of these, the gravimetric method with precipitation of barium sulfate is the most accurate; however, it is also time consuming and has limited sensitivity. Further, barium sulfate has a distinct tendency to form poorly behaved precipitates that hold occluded water readily, making the weighing operation something less than ideal. The turbidimetric method, in which barium sulfate is formed as a colloidal suspension and its absorbance measured, is generally used in lower concentration ranges. This method is faster than the gravimetric method and more sensitive, but its accuracy and reproducibility seem to depend rather heavily on the analyst's skill. In addition, the method is poorly suited to waters that have significant suspended material or color. A number of volumetric methods have been proposed for the determination of sulfate but as yet seem to be of questionable value for the analysis of potable waters.

Although the gravimetric method is far from ideal, it is the most reliable approach currently available. The sensitivity limit of the method and the analysis time are partially set by the need to weigh the precipitate. The incorporation of radiotracer techniques[1-6] into a basically gravimetric procedure can, in favorable cases, preserve most of the advantages of the method but at the same time eliminate the need for the final weighing. The use of $^{133}BaCl_2$ in this case makes it possible to count the final barium sulfate precipitate instead of weighing it. Furthermore, the amount of ^{133}Ba left in the supernatant after filtration is related

*School of Civil Engineering and Environmental Science, University of Oklahoma, Norman, Okla.

to the sulfate concentration; so counting of an aliquot of the supernatant, with proper calibration, gives another measure of the sulfate concentration. In this case, a constant amount of labeled barium chloride solution would be added to a series of samples. Obviously the determination of a counting rate is only a relative measurement; both precipitate counting and supernatant counting procedures have to be calibrated.

PROCEDURE

Reagents and Solutions

If the sulfate samples (or standards) have a range of 0 to 500 mg/liter and if a two-fold excess of barium is appropriate at 500 mg/liter sulfate, then approximately 5 g/liter of reagent-grade $BaCl_2$ is satisfactory. Obviously this solution does not have to be standardized independently.

The amount of ^{133}Ba that needs to be added to the stock solution must be estimated. For a desired counting rate for the supernatant of 5000 counts/min at 500 mg/liter sulfate and an overall counting efficiency of 0.5, calculations indicate 5 to 10 μCi/liter of ^{133}Ba should be satisfactory. This was found to be the case for the procedure given below.

The generally licensed amount of ^{133}Ba is 10 μCi. If the stock solution is made up with 5 μCi/liter, this would be enough for 200 determinations. Actually, the 5000-counts/min value is a minimum value, and the counting rate will increase for samples with a sulfate concentration less than 500 mg/liter. Hence the specific activity of the stock solution could be decreased by a factor of 2 or 3 without serious damage to the procedure; however, longer counting times would be needed.

The standard (known) solutions can be made up readily from reagent grade sulfuric acid. They can be standardized in a number of ways, including titration with primary standard sodium carbonate.

Since this work involved a comparison to established techniques, reagents and solutions were prepared as suggested by the American Public Health Association's standard methods.[7] Two procedures were studied. In one, the precipitate was counted, and in the other, an aliquot of the supernatant was counted.

Procedure Used to Determine 0 to 500 mg/liter Sulfate

1. Place 25 ml of sample (unknown or standard) in a 50-ml beaker.
2. Add 2 drops 1:1 HCl.
3. Heat to just below boiling.
4. Add 10 ml labeled $BaCl_2$ solution ($^{133}BaCl_2$) with stirring.
5. Digest precipitate at 70 to 75°C for 30 min.
6. Cool to room temperature.
7. Filter with 0.45-μ membrane filter paper, using suction. Catch filtrate in a 50-ml centrifuge tube. Do not wash precipitate at this stage.
8. Remove centrifuge tube from filtration assembly, and adjust volume of supernatant to 35 ml. All supernatants must be brought to the same volume after evaporation to replace losses during evaporation, otherwise the counting rate of a given volume of supernatant is not simply related to the sulfate concentration of the sample.
9. Count 5-ml aliquot of supernatant in well scintillation system.
10. Wash $^{133}BaSO_4$ precipitate on filter paper with three to four small volumes of benzene and air-dry precipitate. The precipitate does not have to be dried to a constant weight. Since ^{133}Ba is a gamma emitter, small and variable amounts of moisture in the sample should not cause a significant lack of reproducibility due to variations in self-absorption.
11. Mount and count the precipitate with a flat-crystal scintillation assembly. The unevenness of precipitate deposition will affect the geometry of counting. This effect can be minimized by counting each sample four times, with 90° rotation of the sample. An average of the four counting rates should be used as the counting rate of the sample. This is especially important for low-sulfate samples where the amount of precipitate will be small.
12. With the appropriate calibration curves, determine the sulfate concentration from the counting rate.

Since the procedure stipulates that a constant amount of $^{133}BaCl_2$ solution is added to all samples (or standards), the sum of the counting rates of the supernatant and precipitate ideally would be a constant for a given $^{133}BaCl_2$ solution. However, since self-absorption, scatter, etc., of a radioactive sample is always a factor, the sum will not be a precise constant but show a gradual decrease as precipitates from samples of progressively higher sulfate concentration are counted.

CALIBRATION CURVES

Typical calibration curves are shown in Figs. 1 and 2. Such curves can be conveniently summarized by

least-square regression equations that were calculated from the data of Fig. 1:

$Y(\text{mg/liter } SO_4^{2-}) = 501 - 0.0160x$ (counts/min/5ml) for supernatant counting

$Y(\text{mg/liter } SO_4^{2-}) = 6.8 + 0.0201x$ (counts/min) for precipitate counting

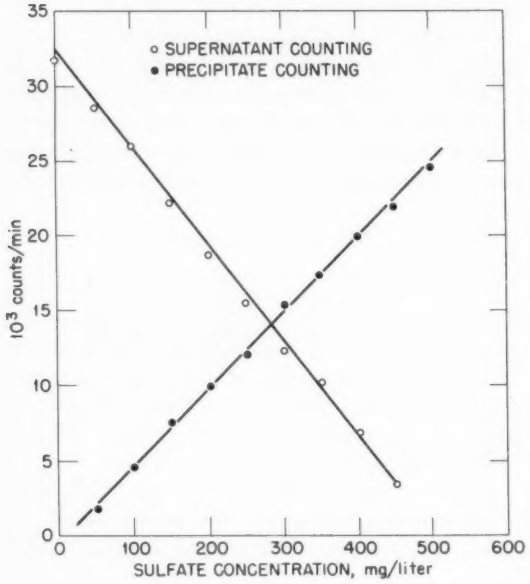

Fig. 1 Calibration curve. ○, supernatant counting; ●, precipitate counting.

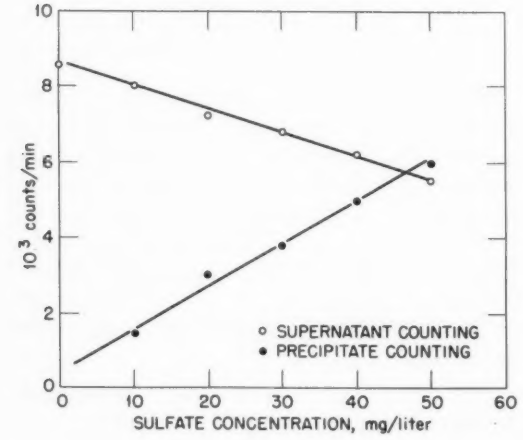

Fig. 2 Calibration curve—low range. ○, supernatant counting; ●, precipitate counting.

Further statistical analysis indicated that counting the supernatant gave better reproducibility than did counting the precipitate. The main reason for this is that counting of solid samples in an "end-on" configuration is generally less reproducible than counting liquids in a well-crystal assembly. At the same time, supernatant counting is faster and less demanding in technique.

COMPARISON OF METHODS

To aid in the comparison of accuracy and precision of the radiometric method with the classical gravimetric method, a series of standard samples was made up with dilute sulfuric acid and analyzed by each method. The results are shown in Table 1.

Table 1 Comparison of Supernatant Counting with Gravimetric Analysis

Standard, mg/liter	Supernatant counting, mg/liter	Gravimetric analysis, mg/liter
250	253	251
250	252	254
250	253	254
200	210	203
200	209	203
200	209	203
100	104	100
100	106	100
100	102	101
50	52	48
50	49	49
50	48	50

In a second study, a series of sulfate solutions was made up using Hach Chemical Co. standards. They were then analyzed by the turbidimetric method as outlined in the standard methods publication[7] and by the radiometric method in which the supernatant was counted. The results are given in Table 2.

In a third study, samples of treated water were obtained from several locations in Oklahoma. The samples were analyzed for sulfate by the gravimetric method, the turbidimetric method, and the radiometric method (supernatant counting). Results obtained are given in Table 3.

A few words about radiological safety are in order. The $^{133}BaCl_2$ solutions contained about 5 μCi/liter, and 10 ml, or 0.05 μCi, was used per sample. This is

Table 2 Comparison of Supernatant Counting with the Turbidimetric Method

Standard, mg/liter	Supernatant counting, mg/liter	Turbidimetric method, mg/liter
50 ± 5	50	49
	50	48
	50	49
40 ± 5	41	42
	43	42
	43	42
30 ± 3	34	34
	34	34
	32	32
20 ± 2	24	20
	24	18
	26	18
10 ± 1	12	7.5
	14	8.5
	13	7.5

well below the value generally associated with significant health hazard, and only routine laboratory precautions are necessary for safe operation. No special shielding or remote handling equipment is needed. In this work, all liquid wastes were evaporated to dryness and treated as dry waste along with the precipitates. Normal low-level radioactive-waste-disposal procedures were used.

Table 3 Comparison of Analytical Methods Using Samples of Treated Water

Location	Gravimetric method, mg/liter	Turbidimetric method, mg/liter	Radiometric method, mg/liter
Midwest City	7	0	0
Shawnee	16	13	10
Purcell	38	33	36
Pauls Valley	53	48	40
Anadarko	130	115	122
Bethany	167	155	154
El Reno	205	186	196
Chickasha	521	465	490

In conclusion, the simple radiometric procedure outlined promises a valid method for sulfate determination. It seems to have accuracy and precision comparable to more classical methods. Further, it is faster and more sensitive than the gravimetric method and probably more objective than the turbidimetric method. The "resolution" of the method (change in counting rate per unit change in sulfate concentration) can be manipulated by changing the specific activity of the $^{133}BaCl_2$ solution.

The radiometric method should not be affected significantly by the presence of color or reasonable amounts of turbidity in the samples as is the turbidimetric method. Since the chemistry is the same, the radiometric method will have much the same interferences as the gravimetric method. These interferences should be minimized by using an average of the concentration values obtained by precipitate and supernatant counting. (RHL)

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Use of Radioisotopic Neutron Sources for Process-Control Activation Analysis

By J. Kuusi*

Supplementary Keywords: *chemistry, analytical; measurement and control system; industry, primary metal; source, neutron; comparison; ^{241}Am; Si; Cr; Al.*

Abstract: *Neutron activation using a radioisotopic source for the determination of chromium in process and quality control during ore beneficiation is described. Characteristics of radioisotopic neutron sources are reviewed, and other potential applications of these sources are illustrated.*

Neutron activation analysis using a radioisotopic neutron source has considerable potential for industrial application to process and quality control. Certain of the radioisotopes produced in the activation decay by gamma emission, the energy and intensity of which are characteristic for the components of the sample. Since the output of a long-lived neutron source is practically constant with time, errors due to variations in the intensity of the exciting radiation do not occur. Because attenuation of the exciting (neutron) and excited (gamma) radiation is often small in the sample, matrix effects are small, and information may be obtained on a large volume of sample material. The measurement technique is relatively simple even under severe industrial circumstances. The chief disadvantage of the method is the wide variation in sensitivities of the determinations of the elements; hence many elements cannot be determined practically by the neutron-activation technique. However, the technique complements other instrumental methods of analysis because it can be used to determine some important light elements—e.g., silicon, aluminum, and fluorine—which often cannot be conveniently determined by conventional methods under industrial conditions. Because of the heterogeneity of the samples, these analyses would be difficult or impossible with other rapid instrumental methods.

The use of a ^{241}Am–Be neutron source for determining silicon, chromium, and aluminum in a chromium-concentration process is described here. The analyzer was constructed and installed at the Outokumpu chrome-ore-concentration plant in Kemi, Finland, by the Outokumpu Research Laboratory in Tapiola as a joint project with the Reactor Laboratory of Helsinki University of Technology in Otaniemi. An on-line system for automatic control of the dry-magnetic chrome-concentration unit is now under consideration. Other applications for the method may be found in the metal, cement, glass, ceramic, and mineral industries.

*Helsinki University of Technology, Reactor Laboratory, Otaniemi, Finland.

RADIOISOTOPIC NEUTRON SOURCES

Recent progress in the manufacture of transuranium elements,[1] making available relatively high-intensity ^{241}Am–Be and ^{238}Pu–Be sources, development of ^{124}Sb–Be source systems, and the potential commercial availability of ^{252}Cf fission-neutron sources, have increased the potential application of such sources in activation analysis. The greatest drawbacks in industrial applications—the low neutron output and the high price of long-lived commercial sources—will gradually be overcome.

Long-lived ^{241}Am–Be neutron sources ($T_{1/2}$ = 458 years), based on the $^{9}Be(\alpha,n)^{12}C$ reaction, have for several years been the best candidates for most industrial applications. However, recently ^{238}Pu–Be sources ($T_{1/2}$ = 87.4 years) have been adopted because of their smaller volume, lower price for comparable output, and smaller gamma-ray background.[2,3] A typical high-intensity ^{238}Pu–Be source, available on the European market for ~$5000, has an activity of 24 Ci and a neutron output of 5×10^7 n/sec and is 6 cm high by 3 cm in diameter.

Near relatives of these sources—^{242}Cm–Be and ^{244}Cm–Be—have been used.[3,4] However, the short (163 days) half-life of ^{242}Cm makes the ^{242}Cm–Be source—as well as the ^{241}Am–Be–^{242}Cm source produced by irradiation of ^{241}Am–Be sources in a high thermal-neutron flux to increase the neutron output by a factor of 10^3—inconvenient for continuous use. Since ^{244}Cm is comparable to ^{238}Pu as source material for industrial applications, manufacturing costs will determine the choice between these two nuclides.

Adequate neutron fluxes for neutron activation analysis may also be produced by photoneutron sources based on the $^{9}Be(\gamma,n)2\alpha$ reaction. Comprehensive feasibility studies in prototype analyzers with multikilocurie ^{124}Sb–Be neutron sources have been reported.[5,6] In these a thermal-neutron flux of approximately 10^{8} n/(cm^2)(sec) has been established in an irradiation volume of 1 liter with an approximately 7-kCi ^{124}Sb–Be source. Drawbacks are the short half-life of ^{124}Sb (60 days)—which may be partly compensated by replacement of the slab, a straightforward procedure—and the extremely high gamma background from the source.

Some (α,n) sources will continue to be used even when ^{252}Cf sources become readily available. The half-lives of most of these sources are much longer than that of ^{252}Cf (2.6 years), which is a significant advantage in certain applications. Further, the neutrons emitted by these sources have enough energy to activate some important elements—silicon, phosphorus, and iron via (n,p) and (n,α) reactions—which cannot be done effectively with fission neutrons from the ^{252}Cf sources. However, despite the significant development of other types of sources, the actual breakthrough in activation techniques is expected to occur with ^{252}Cf fission sources.[3,7] The availability, as of Feb. 1, 1971, of ^{252}Cf emitting 2.34×10^{6} n/(sec)(μg) at a price of $10 per microgram will make its use economically feasible.[8] Promising results have been reported[9-11] from feasibility studies.

Neutron generators are alternatives to radioisotopic sources for use under industrial conditions. Even though the neutron intensity obtainable with generators is some decades higher than that provided by present radioisotopic sources, their high cost, bulk, and the limited life of target are disadvantages. However, within the next 10 years there will also be progress in the performance of generators, which have the advantage that the radiation hazard is negligible once the current has been switched off. Also, the 14-MeV neutrons from generators produce the (n,p), (n,α), and $(n,2n)$ reactions necessary for determining some important light elements, such as oxygen, more effectively than neutrons from radioisotopic sources. Thus generators should be regarded not as competitors but as complements to radioisotopic sources.

In the analyzer described in this article, a 5-Ci ^{241}Am–Be source with a neutron output of 1.25×10^{7} n/sec was used because plutonium sources were not available when the instrument was constructed. If the price of ^{238}Pu–Be sources decreases appreciably in the near future, as is expected with the increasing production of ^{238}Pu for other purposes, a ^{238}Pu source might be preferable.

APPLICATION TO CHROME-CONCENTRATION-PROCESS CONTROL

Silicon, chromium, and aluminum—particularly silicon—concentrations are very important in the chrome-concentration-process control. The wet-chemical methods for determining these elements are laborious and time consuming, and the heterogeneous and crystallized structure of sample particles typical of the ore makes X-ray-fluorescence analysis for these elements difficult or impossible.

Since the neutron-activation determination of silicon, chromium, and aluminum is a known technique,[12-15] activation analysis seemed to be a solution to this specific problem. After successful laboratory-scale feasibility studies,[16] an activation analyzer[17] was constructed. Silicon is determined from counts accumulated under the 1.78-MeV photopeak in the gamma spectrum of ^{28}Al ($T_{1/2}$ = 2.3 min) produced via the $^{28}Si(n,p)^{28}Al$ reaction by fast neutrons from a ^{241}Am—Be neutron source; chromium from the 1.43-MeV peak of ^{52}V ($T_{1/2}$ = 3.8 min) produced via the $^{52}Cr(n,p)^{52}V$ reaction; and aluminum from the 0.85- and 1.01-MeV peaks of ^{27}Mg ($T_{1/2}$ = 9.5 min) produced via the $^{27}Al(n,p)^{27}Mg$ reaction.

Phosphorus, aluminum, iron, and manganese may interfere with the determination of silicon. However, these elements have only a negligible effect since thermalization of the fast neutron flux is small (and phosphorus is present only in low concentration). The sum peak of 0.85- and 1.01-MeV gamma rays of ^{27}Mg from the $^{27}Al(n,p)^{27}Mg$ reaction and 1.81-MeV gamma rays of ^{56}Mn ($T_{1/2}$ = 2.58 hr) from the $^{56}Fe(n,p)^{56}Mn$ and $^{55}Mn(n,\gamma)^{56}Mn$ reactions cause a small background in the silicon channel, but the effects of these background counts and of those due to the 1.38-MeV gamma rays of ^{24}Na ($T_{1/2}$ = 15 hr) from the $^{24}Mg(n,p)^{24}Na$ reactions in the chromium channel and 0.85-MeV gamma rays of ^{56}Mn in the aluminum channel may be eliminated with appropriate calibration curves.

Analyzer

The analyzer (Fig. 1) consists of three units—an irradiation unit, a detection unit, and an electronic unit. The analyzer system was installed in a control laboratory beside the processing hall, with the detector

Fig. 1 The activation analyzer consisting of the irradiation unit (on the left), the measuring unit (on the right), and the electronic unit (in the middle). The sample-presentation bottle is seen on the measuring unit.

~6 m away from the source to decrease the background due to high-energy capture-gamma rays from the irradiation unit and surrounding materials.

The sample, a dry powder, is poured into a flat Perspex bottle with a cylindrical hole at its axis for the neutron source. The 420-cm^3 bottle is filled with about 980 g of sample, weighed, and passed through a door in the top of the irradiation unit on a sample-presentation lift. The door is closed, and the semiautomatic cycle is started by pressing a key. The lift moves down along the central axis of the unit so that the 5-Ci ^{241}Am–Be source, which has rotated on a shaft from the shielded position to the central axis, goes into the hole in the bottle (Fig. 2). After a predetermined irradiation time, the lift moves up and the source rotates back into the shielded position. The door is opened, and the sample bottle is transferred manually to the measuring unit and placed between two 3- by 2-in. NaI detectors. Counting starts automatically after a predetermined transfer time. Then, after a predetermined counting time, the counts accumulated in the

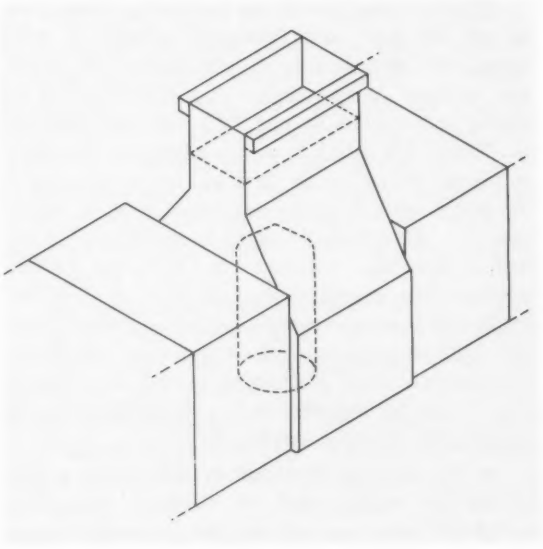

Fig. 2 Analyzer.

silicon, chromium, and aluminum channels selected by three single-channel discriminators are displayed on a tube in the electronic unit, using a selection switch.

Results

Figure 3 shows the gamma spectrums from a chrome-concentrate sample (2.8% SiO_2, 44.5% Cr_2O_3, 13.6% Al_2O_3) and from a sample from a titanium dioxide (pigment) process (4.3% SiO_2, 5.4% Al_2O_3) measured with a multichannel analyzer.

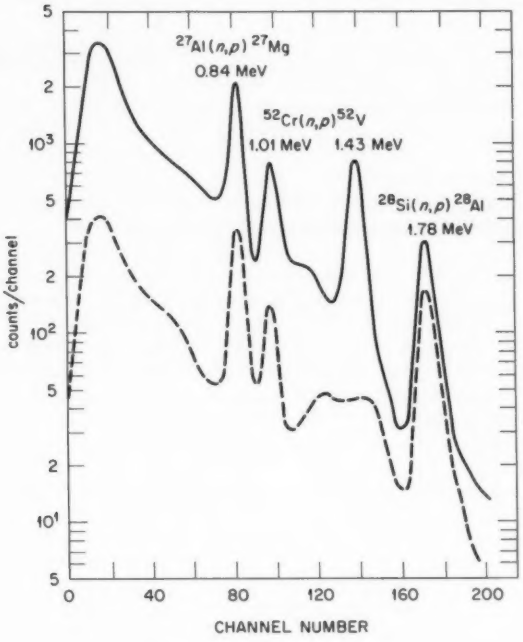

Fig. 3 Gamma spectrums from the analysis of (——) a chrome-concentrate sample and (– – –) a titanium dioxide–process sample.

Figure 4 shows calibration curves for chromium and silicon in chrome-concentrate samples. The counts in the silicon channel were normalized to correspond to the preferred sample weight of 980 g. The statistical error of counting, including errors due to background statistics, corresponds to ±0.09 wt.% SiO_2 when the SiO_2 content is 5 wt.%. Small effects due to the variations in the concentrations of interfering elements can be almost totally eliminated by using the calibration curve because of the systematic nature of these variations in the process samples. When establishing the chromium calibration curve, the counts due to the continuous part of the ^{28}Al spectrum in the chromium channel are subtracted, using the counts accumulated in the silicon channel and a coefficient determined from the pure ^{28}Al spectrum. Since the remaining net counts in the chromium channel were not normalized to correspond to the same sample weight, the calibration curve corresponds to constant-volume samples of varying density and is concave. This procedure gave the best results in this application with this type of irradiation and counting geometry. If the results were normalized to correspond to the same sample weight, the slope of the calibration curve would remain relatively small because the increase in the chromium content is followed by an increase in density concomitant with an increase in the gamma-ray absorption in the sample at this gamma-ray energy. The statistical error of counting, including the effects of background and the subtraction of the continuous part of the ^{28}Al spectrum, corresponds to ±0.5% Cr_2O_3 when the Cr_2O_3 content is 40%.

During the year and a half of routine use of the instrument, several tests have been carried out to check its reliability, especially in silicon and chromium determinations. In one test, three operators (in three separate shifts) with no previous experience in the use of the analyzer independently analyzed samples with the same concentrations. Average deviations of the results of 52 analyses were 2σ in the determination of silicon and 1.1σ in the determination of chromium, where σ means only the standard deviation due to statistical error.

In the determination of aluminum in the chromium concentrates, the statistical error of counting, including the effects of the subtraction of the background and the contributions of the continuous spectrums of ^{28}Al and ^{52}V, corresponds to ±0.13% Al_2O_3 when the Al_2O_3 content is 14% and activation and counting times of 10 min and a transfer time of 30 sec are used.

When ore or, especially, tailings are being analyzed, the statistical error of counting in the determination of chromium is relatively high owing to high silicon and low chromium contents. If greater accuracy is needed, chromium and iron are determined with a radioisotopic X-ray spectrometer having a 10-mCi ^{238}Pu X-ray source, differential filters, and a thin scintillation detector. The statistical error of counting corresponds to ±0.15% Cr_2O_3 in tailings with a Cr_2O_3 content of 6% when a counting time of 1 min per filter is used.

The potential use of the activation analyzer in the control analysis of other types of processes has also been studied. Figure 5*a* shows the results of analysis of cement raw-mix samples and Fig. 5*b* those of samples

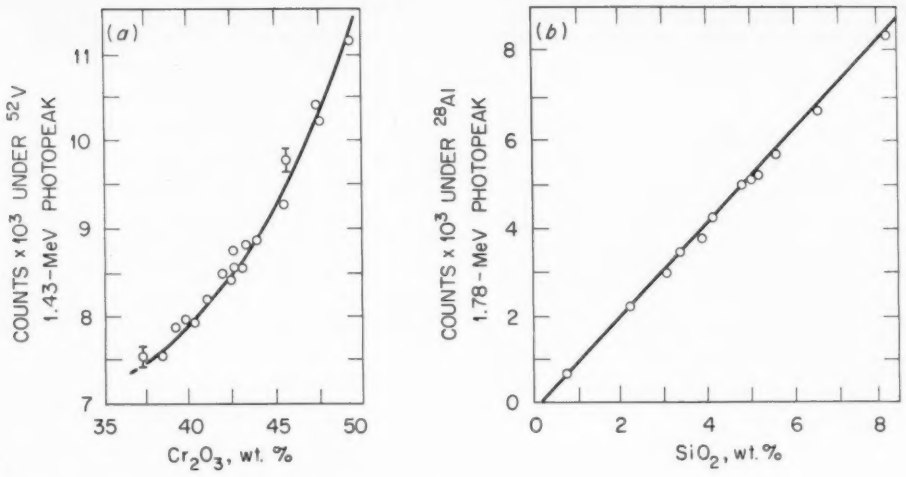

Fig. 4 Calibration curves for the determination of (*a*) chromium and (*b*) silicon in chrome-concentrate samples. Activation time 10 min, transfer time 0.5 min, counting time 10 min. Sample weight varied from 900 to 1100 g.

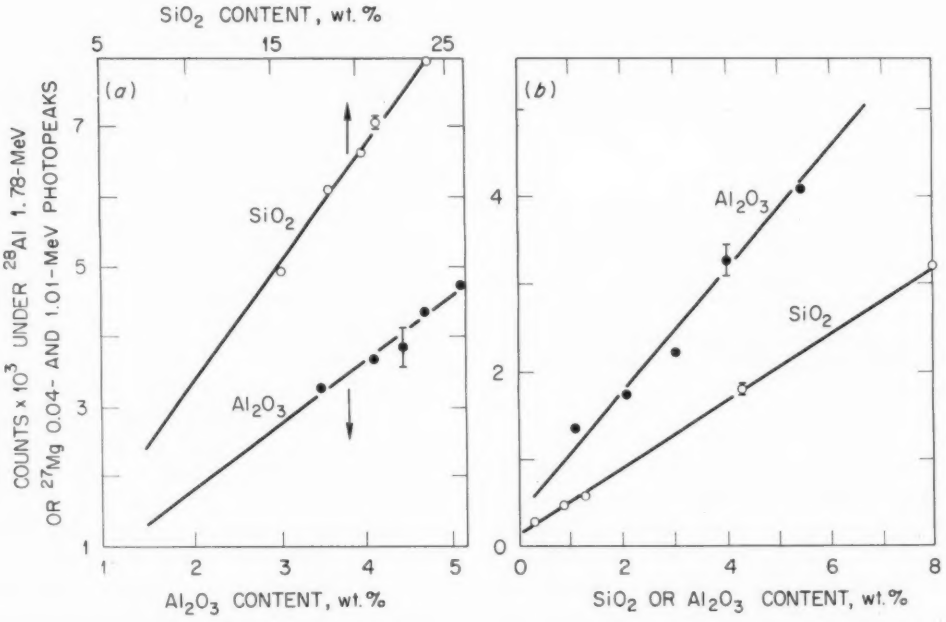

Fig. 5 Results of feasibility studies for determination of silicon and aluminum in (*a*) 515-g cement raw-mix samples from a dry cement-making process and (*b*) in 250- to 345-g titanium dioxide process samples. Activation time 10 min, transfer time 0.5 min, counting time 10 min.

of a titanium dioxide (pigment) process. Silicon and aluminum were determined in both materials with relatively good precision.

An analyzer of this type should have great potential use, especially in controlling modern dry-cement-making processes, where a rapid method for controlling the homogeneity of the raw mix is even more important than in wet processes (where, also, this method of analysis may be used[18]). Positive results have also been obtained in analyzing samples from glass-making processes and from some other metallurgical processes. (MG)

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Activation Analysis of Particulates

Supplementary Keywords: *pollution; chemistry, analytical; atmosphere; reactor; neutron.*

Abstract: *Neutron-activation techniques for determining the composition of atmospheric particulates, developed at two different sites, are described.*

Neutron-activation methods have been developed for determining the composition of particulate contamination of the air. Data on such particulate matter are needed for determining the degree of the hazard they present to the public and for instituting and enforcing

pollution and control measures. Since many of the hazardous materials occur in trace amounts, the analytical method used must be very sensitive. And, because many analyses must be made, often over a wide area, the method must be a rapid one.

Among the groups working on nondestructive, computer-assisted activation analysis of particulate pollutants of the air are those at the University of Michigan and at the University of Missouri. Techniques developed by them are summarized here. (MG)

NONDESTRUCTIVE MULTIELEMENT ANALYSIS OF AIR-POLLUTION PARTICULATES*

By Richard Dams, Kenneth A. Rahn, Gordon D. Nifong, John A. Robbins, and John W. Winchester

A nondestructive and computer-assisted neutron-activation analytical procedure for the determination of up to 33 elements in air particulates was developed at the University of Michigan and tested on samples taken in and near the urban industrial area of northwest Indiana and Chicago. Samples were taken by drawing air through a clean filter or impaction-sampler surface, e.g., cellulose or polyethylene, and were neutron irradiated and counted with minimum interference from induced radioactivity in the filter. Short and long irradiations, gamma spectrometric measurements with a Ge(Li) detector scheduled over a 3-week period, and computer calculations from magnetic-tape records provide the selectivity and simplicity needed for practical application to air-pollution investigations.

*From the Department of Meteorology and Oceanography and Great Lakes Research Division, University of Michigan, Ann Arbor, Mich. 48104; summary of papers presented at the Second International Clean Air Congress, Washington, D. C., December 1970, and at the International Atomic Energy Agency symposium on the Use of Nuclear Techniques in the Measurement and Control of Environmental Pollution, Salzburg, Nov. 26–30, 1970. Present addresses of the authors are, respectively: Institute for Nuclear Sciences, University of Ghent (Belgium); Department of Meteorology and Oceanography, University of Michigan, Ann Arbor; Bethlehem Steel Corp., Bethlehem, Pa.; Great Lakes Research Division, University of Michigan, Ann Arbor; and Department of Oceanography, Florida State University, Tallahassee.

Sampling and Analysis Procedure

Particulates, which occur in the atmosphere mainly in the range 0.1 to 10 μ radius, were sampled efficiently by cellulose-fiber filters or by cascade impactors with polyethylene-film surfaces. Each sample was packaged with a suitable flux monitor or a comparison standard mixture of elements and given neutron irradiations for 5 min at 2×10^{12} n/(cm^2)(sec) or 2 to 5 hr at 10^{13} n/(cm^2)(sec). At 3 min after the first irradiation, a 400-sec count was made and followed by a 1000-sec count, using a 30-cm^3 Ge(Li) detector and a 4096 channel analyzer. At 20 to 30 hr after the second irradiation, a 2000-sec count was made and followed 20 to 30 days later by a 4000-sec count. All data were recorded on magnetic tape for computer data processing. The isotopes and half-lives measured were

First irradiation	Second Irradiation	
	First count	Second count
2.3-min ^{28}Al	15-hr ^{24}Na	83.9-day ^{46}Sc
3.77-min ^{52}V	12.5-hr ^{42}K	27.8-day ^{51}Cr
5.1-min ^{66}Cu	13.8-hr ^{69m}Zn	5.24-year ^{60}Co
9.5-min ^{27}Mg	12.8-hr ^{64}Cu	45.1-day ^{59}Fe
8.8-min ^{49}Ca	35.9-hr ^{82}Br	71.3-day ^{58}Co (from Ni)
15-hr ^{24}Na	26.3-hr ^{76}As	245-day ^{65}Zn
2.85-hr ^{56}Mn	14.3-hr ^{72}Ga	121-day ^{75}Se
54-min ^{116m}In	40.3-hr ^{140}La	260-day ^{110m}Ag
37.3-min ^{38}Cl	47.1-hr ^{153}Sm	60.9-day ^{124}Sb
18-min ^{80}Br	9.35-hr ^{152m}Eu	32.5-day ^{141}Ce
25-min ^{128}I	2.75-day ^{122}Sb	46.9-day ^{203}Hg
5.81-min ^{51}Ti	24-hr ^{187}W	27-day ^{233}Pa (from Th)
5.1-min ^{37}S	2.7-day ^{198}Au	

Tests

The procedure was used for the first major study of trace elements in a large urban area using neutron activation. Therefore three types of samples were taken to assess the value of the method in indicating data of interest: (1) a time series of filter samples taken every 90 min for 34 hr at a rural location generally downwind of the northwest Indiana industrial region; (2) an area-wide group of filter samples taken simultaneously at 25 urban and rural stations in the same region; and (3) particle-size fractions taken by a cascade impactor

at 7 stations within the industrial area. In the time series, large variations in concentration were found and could be correlated with meteorological conditions during the experiment. In the area-wide study, anomalously high concentrations of 10 elements were discovered to be localized within part of the urban area and correlated with certain nearby industries; but other elements, which showed no anomalies, could be ascribed to regional sources, possibly natural. In the particle-size study, some elements typical of dispersion sources of refractory materials were found and may have arisen from high- or low-temperature vapor-condensation processes.

Because of the high quality of data on a large number of elements obtained by the neutron-activation technique, valuable insights into air-pollution processes can be gained which cannot be gained by less sensitive methods frequently used in air-pollution-control laboratories. (MG)

NEUTRON ACTIVATION ANALYSIS OF TRACE ELEMENTS IN AIRBORNE PARTICULATES

By R. F. Tuttle,* J. R. Vogt,* and T. F. Parkinson*

The activation-analysis procedure developed at the University of Missouri was tested in a heavily industrialized and a nonindustrialized area. Air is sampled by passing it through a filter—cellulose, glass fiber, or a commercial product of unidentified composition. The samples were irradiated at a thermal-neutron flux of 3.4×10^{14} n/(cm^2)(sec), and the induced gamma radiations were counted with a NaI(Tl) detector connected to a multiplier phototube. The data were computer processed.

Procedure

The filters were cut into pieces, softened in acetone, folded into a small volume, and placed in a polyethylene irradiation vial. Samples were irradiated for 1 to 2 min and allowed to decay for 3 min before the first count. Subsequent counts were made at appropriate times for determination of the longer lived species.

The data were processed with the Alpha-M code* or a modified version of it, the Ouija. The Alpha-M code was developed for the quantitative analysis of radioactive samples by the least-squares resolution of the gamma-ray scintillation spectrums. The program can handle a very large library of standard gamma-ray spectrums, which are used to resolve the spectrums being analyzed. Corrections can be made for background, counting time, decay time, dead time, gain and threshold shifts (automatic or manual compensation), complement numbers, negative or small positive concentrations, sample fraction, and volume reduction prior to counting. The least-squares method minimizes the statistically weighted sum of squares of the differences between the observed and calculated values. With the availability of high-speed computers, a solution by this method is a relatively simple procedure.

Tests

The validity of the counting and data-analysis procedures was tested in a series of experiments with samples containing known amounts of several radioisotopes (^{60}Co, ^{54}Mn, ^{24}Na, and ^{65}Zn). The measured gamma spectrums were analyzed using the computer code in the same manner as the air-particulate samples. Differences between the known and deduced activities were typically in the range 0.1 to 1.7%.

The procedure was then field tested on samples from a heavily industrialized city and a nonindustrialized community—Cincinnati, Ohio, and Columbia, Mo., respectively. In the samples collected in Cincinnati, the concentrations of Al, Cr, Ca, Cl, and V were comparable with those in the Columbia samples. However, As, Cu, Mg, and Sn were present in the Cincinnati samples in concentrations of 10^{-2} to 10^{-1} μg/cm^3 but were not detected at all in the Columbia samples. That more pronounced differences in the two sets of samples were not evident is somewhat surprising. However, Columbia air has a rather high concentration of suspended particulate matter (54.2 μg/m^3) coming from quarries (60.6%), power plants (30.8%), and vehicles (5.7%).

Identification of the different elemental pollutants with particular sources was not attempted with the few samples available. (MG)

*University of Missouri, Columbia; summary of paper presented at Symposium on the Use of Nuclear Techniques for Measurement and Control of Environmental Pollution, Salzburg, Austria, Nov. 26–30, 1970.

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A Radiotracer Study of the Acidic Hydrolysis of Poly(Methyl Methacrylate)*

By Arthur B. Robertson and H. James Harwood†

Supplementary Keywords: *chemistry, organic; chemistry, physical; kinetics; reaction mechanism; material tracing; comparison;* ^{14}C.

Abstract: *The hydrolysis of poly(methyl methacrylate) samples was investigated by conventional kinetic methods and also by the described double-hydrolysis technique that used* ^{14}C *as a tracer. The results obtained permitted the estimate of the relative reactivities of methyl methacrylate units in isotactic, heterotactic, and syndiotactic environments. This is a condensation of a paper presented at the 161st National American Chemical Society Meeting, Mar. 28 to Apr. 2, 1971, Los Angeles, Calif.*

Studies[1-6] on the hydrolysis of acrylate and methacrylate ester units in polymers suggest that hydrolysis may occur in stages, the initial stage occurring 4 to 10 times as fast as the last initial stage. This effect has been attributed to the initial presence in the polymers of ester units that are in favorable configuration and/or structural environments; these units are assumed to hydrolyze faster than those in less favorable environments.

Most of the information on the hydrolysis of polymers and copolymers containing acrylate and methacrylate ester units has been obtained by kinetic methods. In such studies, it is difficult to separate the influence of specific interactions, such as local configurational effects, from less specific interactions, such as polymer–solvent interactions, hydrophobic bonding, etc. When specific interactions have a dominant influence on the reactivity of ester units in polymers, the hydrolysis behavior should be interpretable in terms of polymer microstructure. Unfortunately, changes in polymer ionization, solvation, and conformation, which occur as hydrolysis proceeds, may also influence the reactivity of remaining ester units, and acquiring precise information about the influence of stereochemical environment on ester reactivity from kinetic studies alone appears difficult.

We have recently described a radiotracer technique[7] that can be applied to studies on the reactivity of groups attached to polymers. The relative amounts and relative activities of groups can be determined with this technique, which is less sensitive than conventional kinetic methods to effects that are related to the extent of reaction.

The ability to impart different levels of activity from ^{14}C to groups with different reactivities in polymer chains is the essential feature of the technique. A polymer (I), depicted below, with uniformly labeled (*) reactive groups is allowed to undergo chemical transformation. After a partial degree of reaction, the proportion of faster reacting groups (F) that have reacted will be greater than the proportion of slower reacting groups (S) that have reacted. If X represents reacted groups, the partially reacted polymer can be represented by II. Now, if the X units can be reconverted quantitatively to unlabeled units of the

$$\sim\!F^{*}\!-\!S^{*}\!-\!F^{*}\!-\!F^{*}\!-\!S^{*}\!-\!S^{*}\!-\!S^{*}\!-\!F^{*}\!-\!S^{*}\!-\!F^{*}\!-\!F^{*}\!-\!F^{*}\!-\!S^{*}\!-\!S^{*}\!-\!F^{*}\!-\!F^{*}\!-\!S^{*}\!\sim \quad (9F^{*}, 8S^{*}) \qquad \text{(I)}$$

$$\downarrow$$

$$\sim\!X\!-\!S^{*}\!-\!F^{*}\!-\!X\!-\!S^{*}\!-\!S^{*}\!-\!S^{*}\!-\!X\!-\!S^{*}\!-\!F^{*}\!-\!X\!-\!X\!-\!X\!-\!S^{*}\!-\!F^{*}\!-\!X\!-\!S^{*}\!\sim \quad (7X, 3F^{*}, 7S^{*}) \qquad \text{(II)}$$

$$\downarrow$$

$$\sim\!F\!-\!S^{*}\!-\!F^{*}\!-\!F\!-\!S^{*}\!-\!S^{*}\!-\!S^{*}\!-\!F\!-\!S^{*}\!-\!F^{*}\!-\!F\!-\!F\!-\!S\!-\!S^{*}\!-\!F^{*}\!-\!F\!-\!S^{*}\!\sim \quad (6F, 3F^{*}, 7S^{*}, 1S) \qquad \text{(III)}$$

(Activity of F units = $\frac{3}{9}$ of original activity; activity of S units = $\frac{7}{8}$ of original activity)

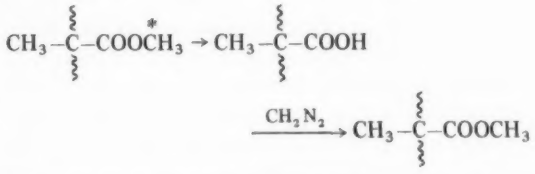
*Condensation of paper presented at the 161st National American Chemical Society Meeting, Mar. 28 to Apr. 2, 1971, Los Angeles, Calif.

†Institute of Polymer Science, University of Akron, Akron, Ohio 44304.

type initially present in the polymer, then the regenerated polymer (III) will contain groups with different levels of activity, depending on their relative reactivities and the conversion obtained in the first transformation. The correspondence of activity loss with conversion for the "reconstituted" polymer (III) can be studied to obtain information about the relative amounts and/or relative reactivities of various types of groups present.

SUBSEQUENT STUDY

The method was applied to the study of the acid-catalyzed hydrolysis of poly(methyl methacrylate) (PMMA) because its microstructure can be defined by NMR (Nuclear Magnetic Resonance) and because the following transformations can be effected



The hydrolysis of poly(methyl-^{14}C methacrylate) samples was investigated by conventional kinetic methods and also by the described technique, which is termed the "double-hydrolysis" technique. The results obtained permit the estimate of the relative reactivities of methyl methacrylate units in isotactic, heterotactic, and syndiotactic environments.

EXPERIMENTAL

A series of polymer samples of different tacticity was prepared from methyl-^{14}C methacrylate using a variety of polymerization techniques. Polymer tacticities were determined by NMR, using the method of Bovey.[8]

Hydrolysis (actually solvolysis) was conducted at reflux (115°C) in a mixture of acetic acid (35 g/g polymer), sulfuric acid (6.1 g/g polymer), and water (3.1 g/g polymer). Samples were removed during the hydrolysis, and the partially hydrolyzed polymers were isolated by precipitation with water. They were then purified by reprecipitation from tetrahydrofuran with water and hexane.

Partially hydrolyzed polymers were reesterified with diazomethane using a technique similar to that of Katchalsky.[9] Reesterified polymers were purified by reprecipitation followed by freeze-drying from benzene. The NMR spectrums of the reesterified products indicated that they had the same tacticities as the starting materials.

Carbon-14 activities of the original and remethylated polymers were determined by liquid-scintillation counting. Sample size (0.01 to 0.05 g) was chosen to give at least 1000 counts/min above background. Each sample was counted for 5 min in triplicate, and the results were averaged.

Conversions in hydrolysis experiments with uniformly labeled polymers (type I) were determined from the residual activities of hydrolyzed polymers that had been reesterified with unlabeled diazomethane. Radioassay proved to be a more sensitive technique for determining conversion than previously used methods,, e.g., conductimetric titration.

Conversions obtained in hydrolysis experiments with nonuniformly labeled polymers (type III) were determined from conversions obtained in parallel experiments with uniformly labeled polymers of the same tacticity.

RESULTS

Detailed kinetic and double-hydrolysis studies are presented in the original paper. The results of the latter study show that the ester units in isotactic triadic environments are 16 and 43 times more reactive than units in heterotactic or syndiotactic environments, respectively. The reactivities of the ester units appear to be dependent only on the relative configurations of nearest neighbors and not on the nature of more remote units. A chain conformational effect may enhance somewhat the reactivity of isotactic units in long isotactic sequences, but the effect is a small one. No satisfactory explanation for the high reactivity of the units in isotactic triads is offered, but it may be related to favorable steric or intrachain solvation effects associated with conformations available to the isotactic configuration. (REG)

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Report on Needs for Standard Radioactive Materials*

Supplementary Keywords: *standards; medicine; industry, nuclear energy; industry, radioisotope; radioactive decay.*

Availability of a wide range of accurate radioactivity standards is a basic necessity for nuclear research, safe application of radionuclides in medicine and technology, and radiation protection of the public. After dissatisfaction with current standards was expressed, an ad hoc panel was organized under the auspices of the National Research Council to determine the need for radioactivity standards in the United States. The text of the panel's report is summarized here.

The panel acquired information from a questionnaire, discussion among its members, presentations to the panel by users and producers of standards, and direct interviews with some users by the panel's secretary. Some results of the questionnaire and interviews are shown in Tables 1 and 2.

The greatest interest was shown in standards in aqueous solution—pure radionuclides accurately measured in terms of disintegrations per unit time. A need was also indicated for solid and point sources whose strengths are expressed in terms of number of particles or quantums of a particular energy emitted per unit time. Standardized solutions must be distinguished from routinely measured solutions; a certificate of description giving degree of accuracy, purity, standardization technique, and assumptions about decay scheme should accompany the standard. Preparation of standards requires considerable time, dedication, and continuity of effort. Experts can prepare most radioactivity standards to an accuracy of 0.1 to 1%; competent workers can achieve 1 to 5%.

Radioactivity standards are used chiefly to calibrate radiation-detection instruments. Fields in which measurements by instruments must be especially reliable include public health, medicine, and nuclear science. The radioactive content of effluents, materials handled by workers, and even food and water must be known to ensure public health. Millions of patients are given radioisotopes annually, and diagnosis and therapy must use only the lowest feasible radiation exposure to the patient. In nuclear science, measurements of nuclear properties require highly precise standards.

Radionuclide sales were about $66 million in 1969. Accurate measurements by suppliers are especially important to purchasers who rely on the supplier for this information.

The National Bureau of Standards (NBS) is established by law as the sole source of federally certified standards. The Radioactivity Section of NBS, which has done its work well, distributes 15 radionuclides as solution standards and 13 radionuclides in other forms, calibrates (for a fixed fee) 31 radionuclides in terms of descriptions submitted by requestors, performs nonroutine calibrations at cost, and develops reference materials to meet national needs. Eleven commercial firms supplied a significant number of radioactivity standards in the United States in 1969. Foreign suppliers include the International Atomic Energy Agency (IAEA), The Radiochemical Centre (England),

*National Uses and Needs for Standard Radioactive Materials, A Report by an Ad Hoc Panel of the Committee on Nuclear Science, National Research Council, National Academy of Sciences, Washington, D. C., 1970; a limited number of copies of this report are available from Division of Physical Sciences, National Research Council, 2101 Constitution Ave., Washington, D. C. 20418.

Table 1 Case Histories on Unsatisfactory Standards

Reported by	Nuclide	Problem
Federal agency	Various	Set of 8; −69% to +141% of rated values; 2 within stated accuracy
Federal agency	^{57}Co	3 suppliers, certified to 3 to 6%; 25% spread
Federal agency	^{137}Cs	0.01 to 1 μCi desired; 3 suppliers tried, 1 succeeded
Federal agency	Various	6 custom ordered; 2 off 50%
Federal agency	Alpha	Contamination with $\beta-\gamma$ activity
Private company	^{95}Zr	Ordered ^{95}Zr, received ^{95}Nb
Private company	^{58}Co	Certified 3%, off 15%
State hospital	Various	Wrong nuclides sent
State hospital	^{51}Cr, ^{32}P	Off 10-fold
Federal contractor	^{226}Ra	Supplier said "as ordered," refused to give assay method, etc.
Federal agency	^{131}I (μCi)	Sent ^{32}P at mCi level instead
Federal contractor	^{35}S	3 suppliers, 11% spread; certified to 5 to 10%
Federal contractor	^{110m}Ag	Predominantly ^{108m}Ag; replacement, two bottles, 42% difference

and the Radiation Measurement Laboratory (France). The IAEA standards are of very high quality and low cost. The English and French laboratories each offer more than twice the number of standards offered by NBS. Users have complained specifically about the small number of standards offered by NBS and about the unsatisfactory accuracy of the standards offered by commercial suppliers. The Radioactivity Section of the NBS offers as few standards as it does because it has insufficient financial support; a substantial part of the preparation cost must be recovered through sales. On the other hand, the cost of maintaining a large staff for preparing standards may be uneconomical for commercial suppliers in the United States.

Table 2 Radioactivity Standards Most Requested

^{125}I	^{207}Bi
^{133}Xe	^{56}Co
^{99m}Tc	^{58}Co
^{51}Cr	^{152}Eu
^{75}Se	^{154}Eu
^{99}Mo	^{26}Al
^{236}Pu	^{252}Cf

The panel made the following recommendations. There should be one government agency as central supplier of radioactivity standards, logically the NBS. The supplier should provide standards at 1 to 3% accuracy and perform research and development at higher accuracy. The supplier should be funded on the basis of needs for standards that transcend short-term financial balances; support should come from such agencies as the U. S. Atomic Energy Commission, Public Health Service, National Science Foundation, and NBS. The supplier should actively advertise availability of its standards and undertake an active program to aid users of standards with training courses and other services. The U. S. Government should encourage use of radioactivity standards for public and occupational health protection. Commercial suppliers should be encouraged to specialize in unusual standards, standards of 3 to 10% accuracy, and calibrated sources; careful certification of these standards, with traceability to NBS calibrations, would be necessary.

(FEM)

Radioisotopic Tracer Determination of Flow Rates and Patterns in Tertiary Waste-Water Treatment

By Harry J. Eby* and Paul E. James*

Supplementary Keywords: *waste and water treatment; pollution; agriculture; dairy;* ^{82}Br.

Abstract: *The use of* ^{82}Br *to determine the flow rate and pattern through a hydroponic bed fed by the effluent from a dairy-waste-disposal lagoon is described.*

Lagoons for collecting livestock and poultry manure and sewage have become popular as a means for disposing of solid and liquid organic wastes. Since the effluent from these lagoons is rich in plant nutrients, it can be fed to a hydroponic bed for the dual advantage of purifying the effluent and producing a crop[1] (Fig. 1). The effluent must flow through the hydroponic system at a uniform rate and distribution so that all plants have access to the nutrient supply for the same length of time. Therefore, when spotty growth of a forage crop growing on a test hydroponic bed fed by the effluent from a dairy-waste-disposal lagoon indicated the need for bed modifications, flow rates and patterns through the bed were determined to see where modifications were needed. A radioisotopic tracer was used in this study because of the convenience and speed with which flow measurements can be made. The tracer test is described here.

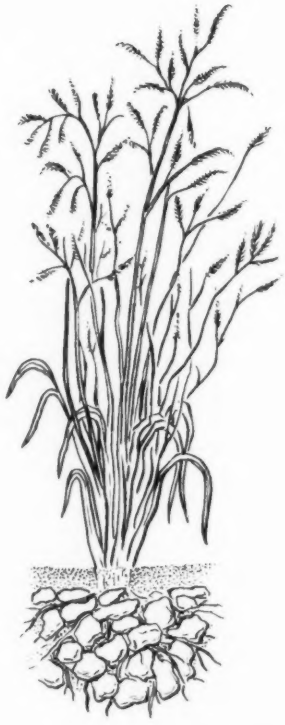

Fig. 1 Grass roots growing between crevices of the crushed rock in a hydroponic bed mechanically filter out solid particles and extract nutrients to feed the plant.

TEST DESCRIPTION

The hydroponic bed tested, which is fed by a 0.375-hectare dairy-waste-disposal lagoon, is a trench 38 cm deep, 2.13 m wide, and 18.3 m long, lined with 10-mil-thick black polyethylene film. Fescue grass is grown in the bed, growth being best in the first 9 m from the inlet. The surface layer is 5 to 7 cm of quartz sand, which provides a germinating layer for the grass seed, and the lower layer is 31 cm of 1.9-cm gravel, which anchors the roots. The trench slopes 7 cm from inlet to outlet.

The flow rate into the bed was set at 10^3 gal/day (3752 liters), roughly equivalent to a flow rate of 10^5 gal per acre of surface (900 thousand liters/hectare), with a 5-day retention time. At the inlet a perforated box distributes the effluent across the bed width, and at the outlet a similar perforated box, reversed, collects the effluent. This liquid is conducted to a stream that eventually reaches a reservoir for public water supply. Bed drainage is provided by a movable pipe that can be lowered or raised to regulate the liquid depth in the bed.

*Livestock Engineering and Farm Structures Research Branch and Crop Production Research Branch, respectively, Agricultural Engineering Research Division, Agricultural Research Service, U. S. Department of Agriculture, Beltsville, Md. 20705. Summary of paper presented at Symposium on Nuclear Techniques and the Fight Against Pollution, Salzburg, Austria, November 1970.

Grass growing in the bed had been planted in May, and one cutting had been harvested when the tracer study was conducted in November (temperature 11 to 13°C). During the test the drain pipe was set in its normal position for the proper liquid depth to maintain a normal flow rate. However, when the radioactivity approached the outlet, the flow into the bed was stopped, and the drain pipe was raised until the isotope had decayed sufficiently that there would be no radiation hazard to humans or livestock downstream.

CHOICE OF ISOTOPE

Since the hydroponic bed was designed for a 5-day detention time, the radioisotope had to last long enough to be detected above background radiation after 5 days, and enough had to be present for detection when diluted by the flow. Bromine-82, with a half-life of 36 hr and a 0.78-MeV gamma radiation, was selected for the test. Gold-198 was considered but was rejected because of its tendency to sorb on rocks. Chromium-51 was rejected because its 27.8-day half-life was too long.

TEST METHOD

The ^{82}Br, 14.7 mCi as $K^{82}Br$ dissolved in 37.5 liters of demineralized water, was poured into the distribution box at the influent end of the hydroponic bed. The water level in the box rose about 5 cm when the tracer was added, giving it a slight hydraulic head. A sheet of opaque polyethylene film was then spread over all the open water area containing the tracer to prevent wildlife from drinking or bathing in it. A catwalk was built for use in taking measurements in the center of the bed, and a center line of cord was stretched along the length of the bed to fix the locations for sample removals.

Radiation above the bed was monitored with a survey meter each day before samples were taken in order to determine how far the tracer had traveled and therefore how many samples were needed. Then samples were taken at 3.8, 11.3, and 18.8 cm from the bottom of the bed. At each level, the samples were withdrawn at 30.5-cm intervals both laterally and horizontally between the points of least and greatest advance of the tracer.

The samples were placed in petri dishes, which were brought to the Engineering Laboratory for measurement of their gamma radiation. A NaI(Tl) scintillation counter was used, the spectrometer being adjusted to read all bromine energies within its capabilities. Background radiation was subtracted from all readings, and a ^{82}Br decay factor was applied. The daily fronts of the radioactive tracer are shown in Fig. 2, and a composite pattern of daily flow front and distance traveled by the tracer is shown in Fig. 3.

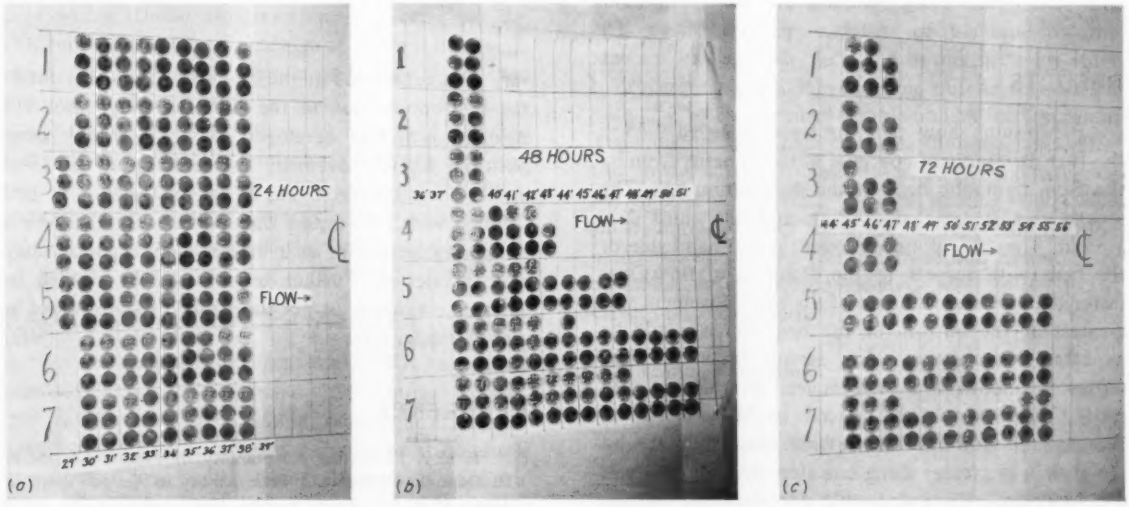

Fig. 2 Daily fronts of radioactive tracer in hydroponic bed. Each of the 55-mm plastic petri dishes contains a 10-ml sample from a specific point in the bed and are placed in a sequential position as to the collection points. Blank spaces indicate that no radioactivity was detected at those points.

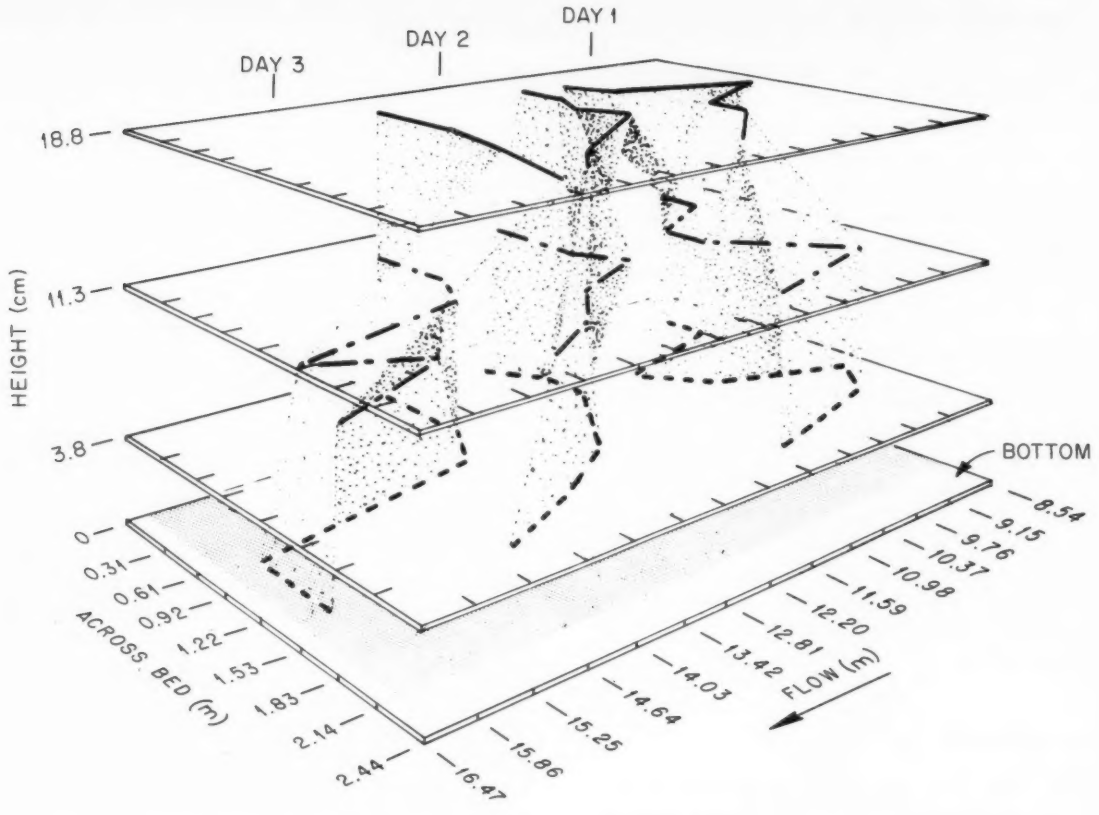

Fig. 3 Composite pattern of daily flow front of radioactive tracer in hydroponic bed. Arrow indicates direction of flow.

RESULTS

The results show that the tracer traveled 9.45 m the first day, probably because of the impetus given by the 5-cm hydraulic head at the distribution box. The second day it traveled 2.13 m, and the third day, 1.85 m. The rate of travel down the left-hand side of the bed (with respect to the direction of flow) was faster than through the rest of the bed. Movement was greatest at the bottom of the bed, which would be expected because the surface against which the flow moves is smooth and there is less interference with roots. Baffles could be placed on the bottom to decrease the flow rate there. What is not clear is why the flow was greater along one side. Possibly this was due to a greater slope along that side, although this was not evident from the construction of the bed.

At the 24-hr sampling time, the wave front was very even (Fig. 2). At 48 hr the front was beginning to vary noticeably, and at the 16-m longitudinal point in the hydroponic bed in the top level of position 7 a stagnant area had developed. At 72 hr at the same position, liquid movement had resumed at the 18-m point. Therefore there was a 2-m-long section of bed through which no liquid was moving. This may be a temporary situation, or a definite septic pocket may have developed. Further tests would be needed to determine whether or not the effluent flow resumed in that particular area. (MG)

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Use of ^{14}C in Studying Pollution of the Air by Petroleum Hydrocarbons

By B. Dimitriades*

Supplementary Keywords: *tracer; material tracing; industry, petroleum and natural gas.*

Abstract: *The interactions in hydrocarbon mixtures and the participation of CO in smog formation were studied using ^{14}C as a tracer.*

The U. S. Bureau of Mines, in a project cooperatively funded by the Air Pollution Control Office of the Environmental Protection Agency, for several years has been studying photochemical smog formation due to automobile emissions. Laboratory studies showed that, of the hydrocarbon contaminants in the atmosphere, olefins and heavy aromatics are the most potent precursors of photochemical smog. In mixtures, hydrocarbons may not react similarly, depending on the presence and nature of component interactions, and therefore interactions of the reacting components must be defined for accurate assessment of hydrocarbon involvement in photochemical-smog production.

A radioactive-tracer technique was selected for the studies because of its sensitivity, accuracy, and specificity. A ^{14}C-labeled vapor in a 100-cm^3 sample theoretically can be detected in a concentration as low as 10^{-5} ppM with a 10-min counting time. For formaldehyde, CO, and CO_2, the chief products of concern here, such sensitivities are several orders of magnitude higher than those achieved in any other method.

The specific phase of the work reported here was a study of component interactions in hydrocarbon mixtures and of the extent of participation of CO in smog formation. For most of the work, the lowest measurable ^{14}C concentration was approximately 10^{-2} ppM.

RADIOACTIVE TRACER STUDIES

For studying the nitrogen oxide (NO_x) sensitized photooxidation of ethylene–^{14}C, 1-butene-1–^{14}C, and isobutylene-1–^{14}C, these compounds were allowed to react with NO_x in a simulated atmospheric environment in a 50-liter chemical reactor. Concentrations of reactants and products were 1 ppM or less. Reaction products of interest were those carrying the terminal double-bonded carbon atom of the reactant olefin—primarily $H^{14}CHO$, ^{14}CO, and $^{14}CO_2$.

The procedures for both preparing the reactants and analyzing the product are described elsewhere.[1] Briefly, for the analysis, the labeled formaldehyde, ^{14}CO, and $^{14}CO_2$ were separated chromatographically, and the carrier gas with the separated components was passed through a microcombustor. Here the olefin and ^{14}CO were converted to $^{14}CO_2$, which was quantitatively collected in a liquid absorber and measured with a liquid scintillation counter. Formaldehyde was separated by passing 80 ml of the reaction mixture through a 1.5- by 0.25-in. glass tube packed with Chromosorb G† wetted with 100 μl of water. The column was subsequently flushed with clean air, and $H^{14}CHO$ was extracted from the packing with a scintillator solution and measured in the liquid-scintillation spectrometer. For total ^{14}C measurement, a sample was passed through the microcombustor where all ^{14}C-labeled compounds were converted to $^{14}CO_2$, which was measured.

Component-Interaction Effects

Component-interaction effects were studied[2] by determining the stoichiometry and kinetics of the NO_x-sensitized photooxidation of 1-butene for the reactant olefin, both alone and in mixture with other hydrocarbons and aldehydes. The butene was labeled with ^{14}C in the terminal double-bonded carbon atom. The stoichiometric measurements showed a wide variation in the extent of olefin reaction with the nature of the companion reactant. The most striking results were those obtained with aldehyde, butene consumption being accelerated by formaldehyde and inhibited by acetaldehyde and propionaldehyde with no significant effect on stoichiometry.

CO in Smog Formation

The observation that the annual buildup of CO in the atmosphere is far less than the amount discharged[3]

*Assistant project coordinator, Bartlesville Petroleum Research Center, Bureau of Mines, U. S. Department of the Interior, Bartlesville, Okla.

†Reference to trade names is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

prompted a search for unidentified processes of CO removal, e.g., in formation of smog in the lower atmosphere and by oxidation to CO_2. The results[4] of irradiating CO with artificial sunlight in the absence and in the presence of other smog-producing compounds—hydrocarbon and nitrogen oxide (NO, NO_2) mixtures, either synthetically prepared or in the form of automobile exhaust—showed that CO participates in smog-forming reactions and is oxidized to CO_2 at a rate equal to 0.1% per hour of exposure to sunlight.

The CO oxidation could not be explained in terms of reaction of CO with oxygen and/or ozone. Reaction with radicals or other reactive species must therefore occur, indicating that CO may be affecting smog formation, for example, through the steps

$$CO + \dot{R}O \rightarrow CO_2 + \dot{R}$$

$$\dot{R} + O_2 \rightarrow R\dot{O}_2$$

$$R\dot{O}_2 + NO \rightarrow R\dot{O} + NO_2$$

This last step—the conversion of NO to NO_2—characterizes smog formation.

The observed rate of CO oxidation would more than account for the suspected disappearance of CO from the atmosphere. In fact, on the basis of present data, CO lifetime in the atmosphere is calculated to be 0.3 year, a value that appears to be more reasonable than the 2.7-year value previously obtained.[5] (MG)

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Isotopes and Moon Rocks

Supplementary Keywords: *source, X-ray; space study; geology; geophysics; measurement and control system; X-ray fluorescence; Mössbauer effect; material tracing; molecular structure; activation, neutron; dating; autoradiography; spectrometry; radioactive decay; conference; crystal; differentiation;* ^{57}Co; ^{57}Fe; ^{87}Rb; ^{87}Sr; ^{109}Cd; ^{232}Th; ^{235}U.

Isotopes have contributed important knowledge about the origin, composition, and structure of moon rocks. At the Apollo 11 Lunar Science Conference,[1] papers were presented[2-7] which give results obtained by isotope-ratio measurement, Mössbauer spectrometry, fission- and alpha-track analyses, and X-ray fluorescence.

From the $^{87}Rb/^{87}Sr$ ratio, a 4-mm rock fragment from the lunar soil, Luny Rock No. 1 (10085-LR-1), was found to have a model total-rock age of 4.44×10^9 years compared with $\sim 3.7 \times 10^9$ years for the other crystalline lunar rocks.[2] This rock is an exotic fragment; it is distinguished from the other described Apollo 11 rocks by its mineral phases and their compositions, its bulk chemistry, and its age. The age difference suggests that it may be a nonmare sample.

Mössbauer resonant absorption studies of ^{57}Fe in pyroxenes from the iron-rich specimen 10044-25-P3 revealed magnetic hyperfine splitting at liquid-helium temperature.[3] This result is potentially useful in contributing to a better understanding of the intrinsic atomic organization of pyroxenes and their possible bearing on the crystallization and cooling history of lunar igneous rocks.

Mössbauer spectra obtained with a ^{57}Co-in-Pd source were used to identify the iron-bearing minerals ilmenite, pyroxene, iron spinel, olivine, and troilite in fines and crushed rocks of types A, B, and C.[4] Because magnetite has been sought unsuccessfully by other workers and methods, a magnetic iron spinel was sought in particular. Certain composition trends were

evident. The iron content increases on breakdown of the crystalline rocks; possibly the iron was formed by reduction of FeS, but the increase in iron content is not accompanied by a decrease in troilite content. The Mössbauer spectra of light and heavy fractions from a type B rock show ordered ferrous site populations for the light fraction and disordered for the heavy.

The distribution and quantity of uranium in lunar volcanic rocks (types A and B) were determined from induced ^{235}U fission tracks.[5] Thin polished sections of the rocks were placed in contact with Lexan plastic. The assembly and a uranium standard were irradiated in a thermal-neutron flux. The plastic was then removed and etched, and the induced ^{235}U fission tracks were observed. The uranium was found to be localized in indeterminate interstitial areas of possibly glassy material formed during the last stages of rock crystallization. In highest concentrations (>40 ppM), the uranium seems to be associated with a reddish phase within the interstitial areas. Phases that crystallize from melts which contain ≤1 ppM uranium have very low uranium abundances (≤0.005 ppM). The breccia matrices generally contain 0.3 to 0.4 ppM uranium with local concentrations >50 ppM.

Alpha-particle activity from ^{232}Th and ^{238}U was studied to determine the distribution of thorium and uranium in Apollo 11 samples.[6] Autoradiography, alpha-particle spectrometry, and an electron microprobe were used. Alpha-track autoradiograms revealed a reticulate pattern related to the boundaries of accretionary lapilli that compose the breccia. Thorium in a coarse-grained crystalline rock appears to be concentrated in micron-sized crystals of a zirconium mineral. Alpha count rates showed secular equilibrium in the thorium and uranium decay series.

In a less-direct application, X-ray fluorescence was used; ^{109}Cd was the X-ray source.[7] To test a lava-lake hypothesis, high-temperature high-pressure experiments were made on natural and synthetic samples. Molybdenum capsules were used to contain some of the samples. Contamination of the samples by molybdenum and loss of iron from them were measured by X-ray fluorescence spectrometry. (HPR)

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Atmospheric Tracer Technique Employing ^{85}Kr and Use of This Technique in Defining Puff Dimensions and Transport Speed*

By P. W. Nickola, J. D. Ludwick, and J. V. Ramsdell, Jr.†

Supplementary Keywords: *tracer; material tracing; data handling; atmosphere; meteorology; ^{85}Kr.*

Abstract: *An atmospheric tracer technique has been developed in which ^{85}Kr is released and subsequently monitored on a real-time basis at 64 field stations, located at distances of up to 800 m from the release point and at elevations of up to 21 m. The technique includes both instantaneous- (puff) and continuous- (plume) release techniques. Data from six puff releases are summarized and analyzed. The effective transport height of puffs released at ground level increases with distance*

*Work performed under contract AT(45-1)-1830 between USAEC and Battelle–Northwest.

†Battelle Memorial Institute, Pacific Northwest Laboratory, Richland, Wash. 99352.

but increases least in a stable atmosphere. In stable atmospheres, the growth rate of a puff in the downwind direction continues to be greater than the growth rate in the crosswind direction as the puff travels from 200 m to 800 m from the release point. However, in less-stable atmospheres, even though the downwind dimension remains greater than the crosswind dimension, puffs become more symmetrical in shape as they move from 200 m to 800 m.

One of the primary techniques for a field investigation of diffusion and transport in the atmosphere is the release of a known quantity of a tracer and the subsequent sampling of the atmosphere at downwind locations. Different particulate and gaseous tracers have been used with various degrees of success.[1] Although some field work has included a few samplers recording on a real-time basis, most of the techniques involve collection of a mass of the tracer over some relatively long time (minutes to days), with the subsequent specification of a mean concentration applicable to the entire sampling period.

The development at Pacific Northwest Laboratory of a field tracer system[2] that monitors atmospheric concentrations of ^{85}Kr at 64 field locations on a real-time basis has permitted the investigation of a diffusing cloud of the gas in a much more detailed manner than has heretofore been possible. This inert-gas tracer has minimum interaction with structures, vegetation, and other atmospheric constituents, and it faithfully mimics actual air motions. Further, the system permits generation and real-time monitoring of either an instantaneous puff or of a continuous plume. The simulation of an instantaneous release of a pollutant (as opposed to a longer period or plume release) is an unusual field capability. Although both instantaneous- and continuous-release techniques have been used by the authors, most of the results reported here deal with the less frequently investigated puffs.

Thirteen releases of ^{85}Kr were made in late 1967 to test the feasibility and response of the prototype system. However, the data generated were of such high quality and in such unusual detail that some quantitative analysis of the data has been made.[3-8] Additionally, in view of the paucity of such real-time data in the literature, the measured concentrations and associated meteorological values have been assembled into one volume.[9]

FIELD SYSTEM AND DATA-HANDLING TECHNIQUES

The field grid over which the tracer was released is shown schematically in Fig. 1. A plume or puff of

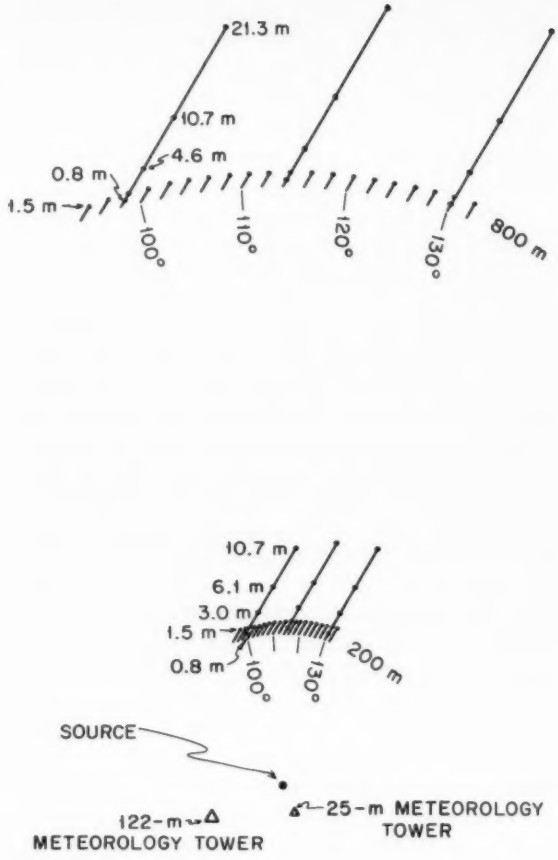

Fig. 1 Schematic representation of ^{85}Kr field diffusion grid.

^{85}Kr was released upwind of two concentric arcs of sampling stations. Vertical profiles of wind and temperature were monitored on two nearby towers. For plume releases, the source was a pressurized-gas cylinder from which krypton was released at a controlled rate of about 1 Ci/min for 10 to 20 min. The effective source height was approximately 1 m. Puffs were generated by crushing quartz flasks containing the tracer in a guillotine-like device. The gas in each flask had been sealed at near atmospheric pressure so as to minimize the initial volume of the "instantaneous point source." Flasks were crushed at ground level.

As the plume or puff was carried downwind, it was detected by a series of 64 halogen-quenched Geiger–Müller (G–M) tubes located on concentric arcs 200 and 800 m from the source point. Twenty of these detectors (Fig. 2), 1.5 m above the ground, were spaced at 2° intervals on each of the sampling arcs. An

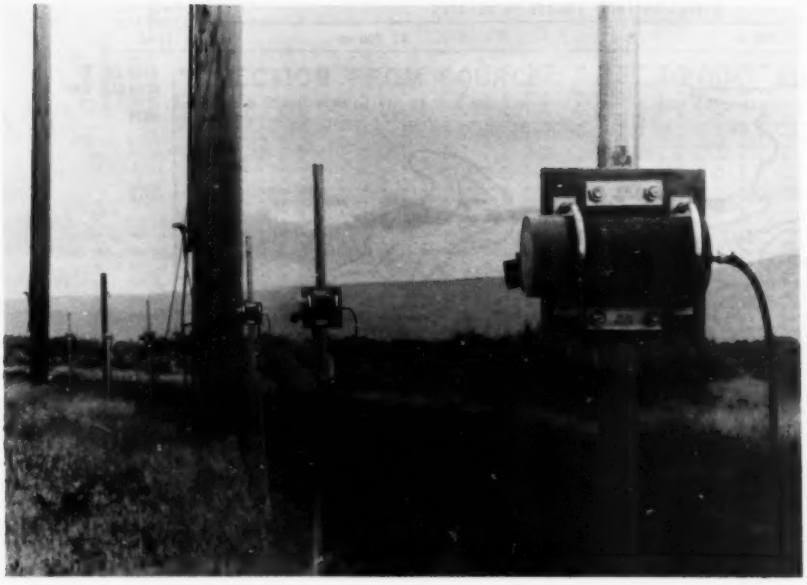

Fig. 2 Field detectors at 1.5-m level. Weatherproof caps protecting mica windows are removed prior to use of system.

additional 24 samplers were mounted at different heights on six towers, three towers on each arc.

Information from these detectors was relayed by coaxial cables to a 4096-address memory programmed to accept data simultaneously from the 64 detectors for 64 time increments. A time-interval selector permitted automatic advance of the stepping process at a slow or fast rate through the 64 time increments. The time-increment selector permitted counting intervals of 1.2, 2.4, 4.8, or 38.4 sec. When the information completely filled the memory, the memory was read out to a unit that provided a photographic reproduction of the counts accumulated in each channel. Data from the photographs were punched into cards for electronic data processing.

Figure 3 shows the printer output resulting from electronic data processing of raw G–M-tube counts of a plume release. Isopleths were added by hand. The numbers plotted are counts per second generated by each 1.5-m-level detector and are directly proportional to krypton concentration. Figure 4 presents concentrations at 200 m resulting from a puff release; the data at the left are from the 1.5-m-level samplers and the data at the right are from the samplers on the tower at 114° azimuth.

RESULTS FROM PUFF RELEASES

The ability to generate instantaneous puffs, combined with the large number of real-time samplers employed with the inert gas-tracer system, affords an opportunity to measure diffusion parameters which generally are not easily measured. Examples of this type of data are downwind and crosswind puff dimensions and the effective height and speed with which the diffusing puffs move.

During the testing of the prototype system, a total of eight puffs was released. Five of the eight puffs moved within the crosswind limits of the sampling stations. A sixth puff remained sufficiently within the grid so that extrapolation of concentration distribution was possible. Six puffs, then, were examined in development of the information which follows.

A portion of the concentration data generated following the release of puff P8* is given in Fig. 4. The left half of this figure shows the relative concentration of krypton for the 200-m arc at an elevation of 1.5 m above the surface. Summation by columns provides the input for determining σ_{yI}, the standard deviation of the distribution of krypton dosage in a crosswind direction, which is also a measure of the size of the puff in a direction normal to the mean wind direction. This crosswind distribution for puff P8 is given in Fig. 5. Summation by rows of the data in Fig. 4 provides a distribution for determining the mean time of passage, T, and the standard deviation of this time. This distribution is given in Fig. 6. If T and its

*Puffs are herein numbered as they were in the published report (Ref. 9).

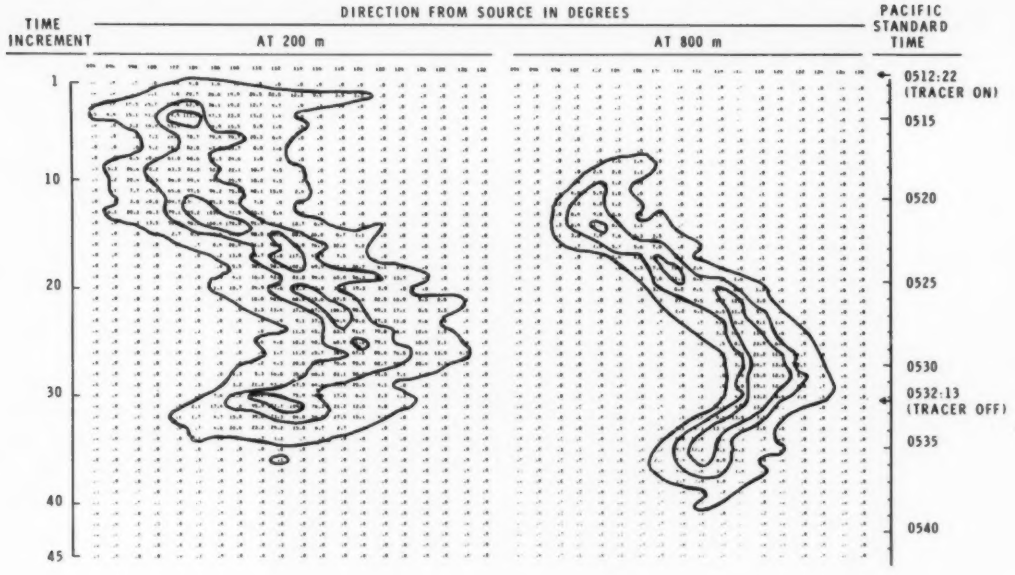

Fig. 3 Distribution of tracer concentration at 1.5-m level with respect to time and direction from source. Tracer released continuously for 20 min.

associated standard deviation are multiplied by an appropriate wind speed, these time parameters become length parameters, and the resulting standard deviation, σ_{xI}, is a measure of the length of the puff in a direction parallel to the mean wind direction.

The problem in this computation is to choose a wind speed which is representative of the puff movement to the specific distances (200 and 800 m) and height (1.5 m) where the measurements took place. Although the 1.5-m wind would seem to be appropriate for computing σ_{xI} values, the correct speed to employ is x/T, where x is the distance of the sampling location from the source. This speed and the associated height of measurement are termed the "effective transport speed," u_e, and "effective transport height," z_e, respectively.

Wind profiles obtained from an instrumented 25-m tower near the source provide the means for determining the effective-height value. Anemometers were mounted at elevations of 0.8, 1.5, 3.0, 6.1, 12.2, and 24.4 m.

Values of u_e and z_e are listed in Table 1. At 200 m from the source, u_e was always less than the wind speed measured at the sampling height (z = 1.5 m), and consequently z_e was always between the sampling height and the release height (z = 0 m). The same statement can be made—except for puff P8—for puffs passing the 800-m arc. The effective speeds and heights increase with distance in all cases. A distance should be reached (and was observed with puff P8) beyond which the centroid of the puff reaching the 1.5-m plane would be transported at a speed and height above that sampling level.

The puffs are listed in Table 1 in order of increasing atmospheric stability. (The criterion used in determining stability was the Richardson number for the layer between 2 and 15 m. It is given in parentheses following the qualitative stability specification.) If a relationship between z_e and stability exists, it is not well defined by these few releases. The tendency might be, on the basis of stable puff P8, an increase in z_e with an increase in stability, but z_e values for the even more stable puff P2 correspond to z_e values for the less stable puffs.

A word concerning the z_e values of 0.5 m for the 200-m arc is in order. The fact that all the extrapolations result in the same value (0.5 m) may be coincidental, but it is not the result of large smoothing procedures. The graphical extrapolation of the measured wind profiles from the lowest anemometer level, 0.8 m, to the 0.5-m level is a relatively straightforward procedure.

Columns headed σ_{xI} and σ_{yI} in Table 1 present physical dimensions of the puffs as measured at the 1.5-m elevation. This elevation is probably not the elevation of the centroid of the puff. The distribution

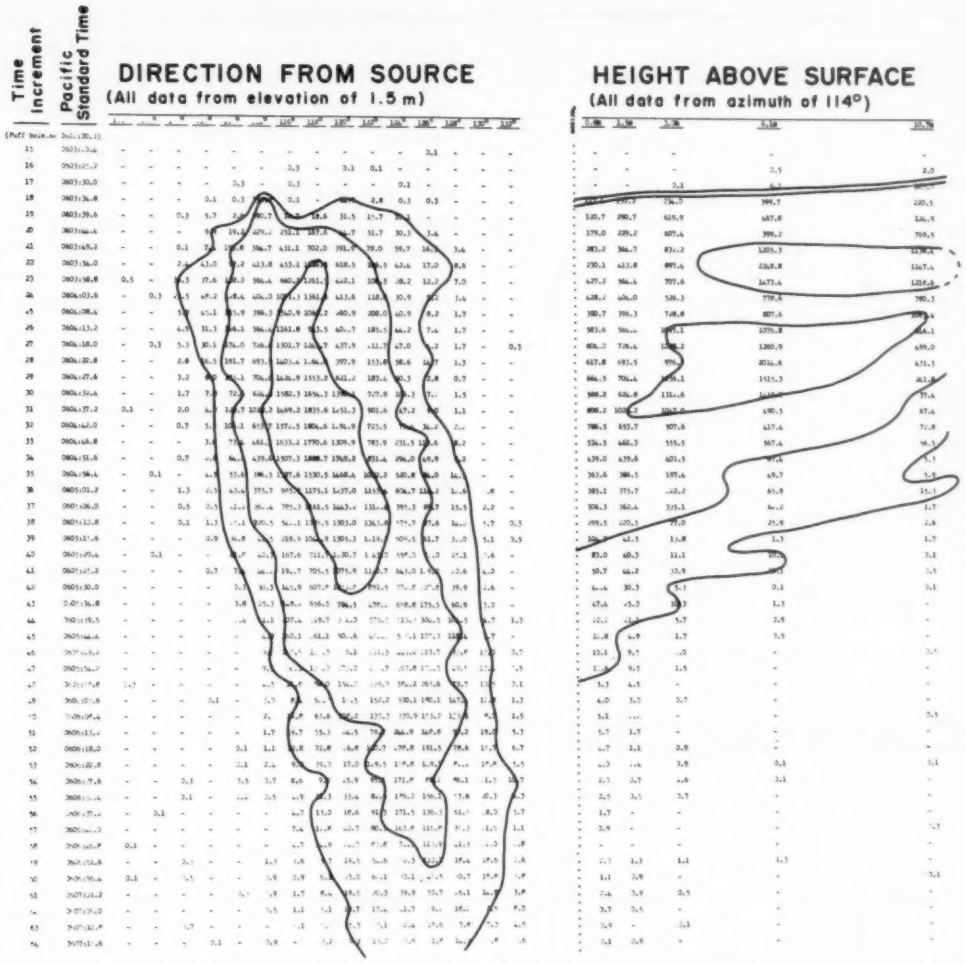
Time Increment
Pacific Standard Time
DIRECTION FROM SOURCE
(All data from elevation of 1.5 m)
HEIGHT ABOVE SURFACE
(All data from azimuth of 114°)

Fig. 4 Distributions of tracer concentration following puff release P8.

of vertical samplers on the current grid is not dense enough to permit specification of the puff centroid. However, because the release and sampling heights are not greatly separated, because the horizontal extent of the grid is limited, and because the effective travel height is usually below the sampling height, the σ_{xI} and σ_{yI} values presented are probably reasonable approximations of these same values for the puff centroid. In any event, direct measurement of puff dimensions—particularly σ_{xI}—are rare, and these values thereby gain in significance

Another method of checking the downwind dimension of the puffs is possible. Since the krypton-concentration data were collected in real time, the downwind dimension of a puff was certain to be at least 600 m if the puff was monitored simultaneously on both the 200- and 800-m sampling arcs. In every instance, the puff was detected by samplers at the 800-m distance before the 200-m samplers had returned to background, although during unstable puff P7, detectors at 200 m were very nearly at background before count rates rose above background at 800 m. At the other end of the scale, during the most-stable conditions, puff P2 was detected simultaneously at 200 and 800 m for more than 12 min.

The ratios σ_{xI}/σ_{yI} in Table 1 are, perhaps, even more enlightening than the data giving absolute dimensions to the puffs. In all instances, the puffs are elongated in the downwind dimension. However, for the unstable-atmosphere test and for two of the three

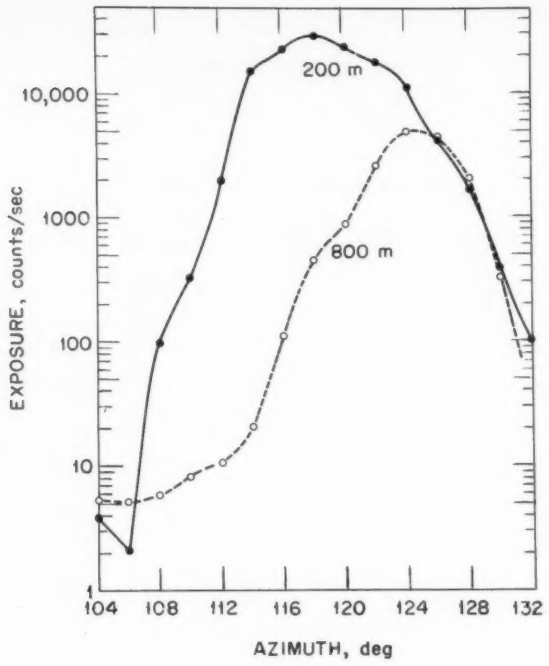

Fig. 5 Crosswind distribution of exposure (concentration time integral) at an elevation of 1.5 m following puff release P8.

neutral tests, comparison of σ_{xI}/σ_{yI} ratios reveals that, during travel from 200 m to 800 m, the puffs became more symmetrical in shape. For the two stable tests, the puffs continued to elongate in a downwind direction. The data suggest that, for ground-level releases, the mechanisms causing diffusion in a downwind direction are always more effective than the crosswind mechanisms for the first moments of a puff's existence. In stable atmospheres, the downwind elongation continues as diffusion continues. In less-stable atmospheres, the downwind and crosswind growth rates approach each other as diffusion continues.

PLANNED IMPROVEMENTS TO SYSTEM

Although this tracer system supplies relatively great detail—especially at the 1.5-m elevation—the 16° interval between towers results in too few measurements to adequately define crosswind concentration distributions above the 1.5-m height. The system is being expanded to include instrumenting of towers spaced at 8° intervals to heights of 27 m at a distance of 200 m, and to 47 m at 800 m. Token installation of samplers at 1600 m is planned for the near future.

The field system is also being altered to avoid the previous limitation of 64 time increments for data

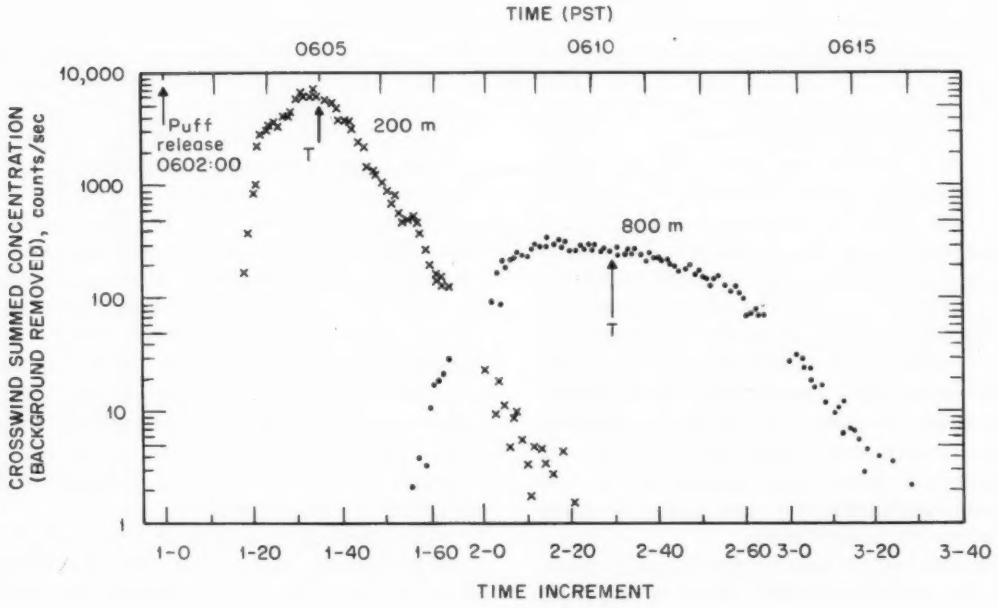

Fig. 6 Crosswind sum of tracer concentration vs. time at an elevation of 1.5 m during puff release P8.

Table 1 Transport and Diffusion Parameters Determined from ^{85}Kr Puff Releases

Test No.	Atmospheric stability	Wind speed at 1.5 m elevation, mps	200 m from source					800 m from source				
			u_e, mps	z_e, m	σ_{xI}, m	σ_{yI}, m	$\frac{\sigma_{xI}}{\sigma_{yI}}$	u_e, mps	z_e, m	σ_{xI}, m	σ_{yI}, m	$\frac{\sigma_{xI}}{\sigma_{yI}}$
P7	Unstable (−0.16)	4.6	3.0	0.5*	32	9.9	3.1	4.0	0.9	75	54	1.4
P6	Neutral (−0.04)	7.3	4.7	0.5*	39	11.0	3.5	6.6	1.1	83	44	1.9
P3	Neutral (−0.03)	4.2	2.5	0.5*	33	12.6	2.6	3.7	1.1	112	28	4.0
P5	Neutral (−0.02)	8.0	5.1	0.5*	40	9.0	4.4	7.1	1.1	95	50	1.9
P8	Stable (0.07)	1.5	1.1	1.0	48	12.1	4.0	1.6	1.8	151	37	4.1
P2	Stable (0.13)	1.2	0.5	0.5*	60	13.8	4.3	1.0	1.1	236	50	4.7

*Extrapolation.

storage. Continuous concentration monitoring will be possible. Furthermore, the incorporation of a computer-compatible magnetic-tape system will eliminate the manual data processing required with the prototype system. (RHL)

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Section

III

Isotopes and Radiation Technology

Food Irradiation

Progress in Commercialization of Irradiated Food

Supplementary Keywords: *food preservation; review, technical; industry, food.*

In a recent article,* Dr. Kevin Shea of the food-preservation section of the Joint FAO/IAEA Division of Atomic Energy in Food and Agriculture, Vienna, reports on new developments in the commercialization of food preserved with radiation. Dr. Shea is on leave from the Division of Isotopes Development, USAEC.

A few countries—Netherlands, Israel, and the USSR—already sell irradiated food in their shops. In Britain, two applications for exemption will be made soon.

The creation of the International Project in the Field of Food Irradiation was inspired by the magnitude of the research needed to obtain wholesomeness data by extensive feeding studies with test animals. In this project, 19 countries have pledged $225 thousand per year for 5 years to support feeding studies. The developing nations, in particular, stand to gain through increases in export trade if irradiation is accepted; India or the Philippines could export insect-free papayas. Switzerland now imports grain to feed dairy cattle. Pesticide residues on the grain are concentrated in some Swiss products, such as cheese and chocolate, to a level above permissible limits for countries that import these Swiss products.

The first of the forthcoming British applications will be to eliminate Salmonellae from frozen horsemeat imported for pet food. Currently, the frozen blocks have to be thawed and heated to rid them of Salmonellae. Gamma rays can penetrate the frozen blocks and kill the microorganisms without thawing the frozen blocks. The second application will be the irradiation of whitefish to extend the shelf life just a few days, which will smooth out the processing at the fishery plant and provide a more even flow of product to the consumer.

Irradiation of food would reduce dependence on chemical additives and cut food losses. The U. S. Food and Drug Administration is carefully considering all aspects of this use of radiation and deserves more sympathetic understanding for its efforts to protect all of us. Two low-dose petitions are planned by the USAEC. Strawberries can be treated to control mold and thus extend shelf life and increase market area. Because of labor problems, a shift to Mexico as the supply source of strawberries is occurring, which makes extension of storage life more important. A second application, which shows great promise, is the use of radiation to both disinfest and extend shelf life of papayas grown in Hawaii. Bromine is usually used to treat against fruit flies, and, because of fruit-fly outbreaks in California, higher permissible pesticide-residue levels have been requested. A dose of only 26 krads will control the fruit fly.

Netherlands is moving ahead with clearances. The importance of making a breakthrough with a popular and profitable product has resulted in mushrooms, asparagus, and cacao beans being emphasized. The first two products respond to low doses by delay in ripening, the last by insect control. The pilot plant at Wageningen has been particularly useful for solving scale-up problems. Israel has test marketed irradiated potatoes and onions, with consumers showing a clear preference for the irradiated foods. Japan plans to submit a petition for clearance to inhibit sprouting in potatoes with radiation. France has granted a temporary clearance for this application, and Spain cleared it over a year ago. The process of commercialization of food irradiation has commenced and will continue slowly, as health authorities grant clearances. The new international program on wholesomeness will assuredly contribute to the acceptance of this method.

(FEM)

*K. G. Shea, Radiation for Fresher Food, *New Scientist and Science Journal*, 1971: 108-110 (Jan. 21, 1971).

A German Evaluation of the Significance of Food Irradiation*

By L. Wiesner

Supplementary Keywords: *industry, food; review, technical; economics; seafood; poultry.*

Food irradiation has been under consideration for about 40 years, but only in the last 10 years has serious process. Health authorities apply the same rules to radiation that they use for the approval of a chemical additive. The harmful effects of excessive concentrations of chemicals can easily be determined, but the analogy of requiring either ingestion of large amounts of an irradiated food or treatment with doses of radiation larger than will be used is not logical. If some of the more sensitive methods and the techniques now being used to examine irradiated food were applied to foods containing approved chemicals, unsuspected harmful effects of necessary additives might well be discovered.

The rejection by the U.S. Food and Drug Administration of the U.S. Army's petition for approval of radiation-sterilized ham was justified, since, in their opinion, the supporting data are inadequate. However, this rejection and subsequent cutbacks in the American food-irradiation program will have serious consequences in Europe. Researchers can no longer expect to obtain American results, and programs already started will probably be curbed.

The approach to approving radiation as a food "additive" has been impractical. For chemical additives, the company hoping to market the additive approaches government authorities for approval and lines up markets, patents, and licensing rights. The expenses of feeding studies can be justified on the basis of the profit expected. But, when a company knows that the process will be available not only to its domestic competitors but also to all foreign competitors, as is the case with irradiation, there is little incentive to spend funds to obtain approval of the process.

A number of countries have now decided that radiation cannot be treated in the same way as a chemical additive. In the Netherlands, animal feeding studies include irradiated food in an amount about equal to the amount normally consumed in a human diet. The bureaucratic processes of approval are quick, and limited amounts of the food can be marketed if no untoward results are observed. Researchers in one country should be able to submit the results of researchers in another country to their governments; the members of the United Nations should work out a suitable procedure for this.

In the Federal Republic of Germany, despite a good transportation system and modern refrigerated distribution units, irradiation of food can still be justified. For example, imported foods such as spices or dried egg powder may not be sufficiently bacteria-free to be marketed without treatment. Other foods may increase in value indirectly after irradiation. Since the freshest fish receives the highest price, German trawlers sometimes return to port with their holds only 50 or 60% full because of the distance of the fishing grounds from Germany. A shipboard irradiation dose of 50 to 100 krads might produce an additional income of 100,000 DM† yearly for this industry by decreasing the time spent traveling back to port and by increasing the sale of fish to inland consumers in Germany and in Switzerland, Austria, Northern Italy, and Eastern France.

Poultry may have its market value enhanced by irradiation. A considerable amount of poultry is preserved by deep freezing, with subsequent organoleptic changes. These changes do not occur in irradiated chickens if process parameters are properly chosen. For fryers, especially, an increase in storage time would allow variations in market demand to have little economic effect.

Potato-sprout inhibition in Germany will probably continue to be primarily based on chemicals, with irradiation being a reserve method, since facilities for irradiation of potatoes would be used only about 2 months a year. Additional products to irradiate, such as strawberries, would be needed to make such a facility economically feasible.

*Based on: Has Food Irradiation Reached Significance Yet? (in German), *Atomwirtschaft*, **15**: 293-296 (June 1970).

†1 DM = $0.273.

For long-term storage, a combination of heat and radiation may be developed which has far less organoleptic effect on a product than a simple heat sterilization. Strawberries held at 98°C for 5 min and irradiated with 100 krads are quite good. Meats and meat products may also be subjected to a combination treatment. Government-maintained reserves for use when supplies are low must be replaced when they spoil; such replacement is costly, and a means of increasing storage time would decrease this expense.

In Europe and North America, where food is abundant and various foods are imported from other regions of the earth, food irradiation is looked on as a means of improving quality and decreasing cost. However, in the developing countries, irradiation of food may be the means of improving the nutrition of millions of people. The Food and Agriculture Organization of the United Nations estimates that 20% of the crop in some countries is lost to microorganisms and insects; in other countries this loss may be as high as 50%. If losses could be halved by irradiation, an adequate diet for 300 million people could be provided at far less cost than an increase in food production to achieve this same end.

To obtain an answer to the question of whether or not food irradiation is significant, the political manner in which the process is restricted must be changed. The immediate consequences of unnecessary delay in the promotion, development, and acceptance of the irradiation process for millions of people are, at the very least, poor health and low productivity because of deficient diet. (FEM)

Effect of Low-Level Irradiation on Fruit*

By E. M. Ahmed and R. A. Dennison†

Supplementary Keywords: *food preservation; industry, food; biochemistry.*

Studies at the University of Florida, utilizing a ^{137}Cs research irradiator, have included the effects of irradiation on citrus respiration and texture modification in strawberries, peaches, and tomatoes. Navel oranges irradiated at 300 krads produced more CO_2 and consumed more O_2 than did nonirradiated fruit during a period of 216 hr after irradiation. Oranges irradiated to 150 krads returned to control levels about 72 hr after treatment. The respiratory quotients (CO_2/O_2) were less than unity when expressed on a volume (ml) basis and approximately unity when expressed on a weight (mg) basis. Marsh seedless grapefruit also showed greater O_2 consumption when irradiated to 300 krads. For Murcott fruit, little difference was detected between irradiated and nonirradiated fruit, although the 150-krad lot did show a slightly higher O_2 consumption.

Varieties of peaches obtained for testing included Redskin, Dixieland, Loring, Maygold, and Suwanee. Sensory evaluation by panel members was confirmed by the following tests: Magness-Taylor measurements, shear press measurements, compression, texture profile evaluation, hysteresis, stress relaxation, creep behavior, and puncture tests. All results indicated that irradiated fruit, as well as ripened fruit, was softer than nonirradiated fruit. Softness was most pronounced immediately after irradiation. Softening as a result of ripening proceeded at faster rates than softening caused by irradiation.

Strawberries were irradiated to 150 and 300 krads and evaluated for texture through tests of penetration, compression, hysteresis, and shear. Irradiated fruit was consistently softer than nonirradiated fruit immediately after treatment. Floradel tomatoes were evaluated for texture through a compression test and through a panel test. For the tomatoes, as with the peaches and strawberries, the flesh was softer in the irradiated than in the nonirradiated fruit.

The conclusion reached from the compilation of data in 94 tables from these tests is that irradiated peaches, strawberries, and tomatoes should be protected during handling, shipping, and storage to a larger degree than nonirradiated fruit. (FEM)

*E. M. Ahmed and R. A. Dennison, Effects of Low Level Irradiation Upon the Preservation of Food Products, USAEC Report ORO-679, University of Florida, May 1970.

†Department of Food Science, University of Florida, Gainesville, Fla.

Radiation Pasteurization of Gulf Shellfish*

Summarized by F. E. McKinney

Supplementary Keywords: *food preservation; seafood; industry, food; biochemistry; food evaluation, subjective; microbiology.*

Abstract: *The results of 8 years of research on the radiation pasteurization of Gulf shellfish are summarized. Researchers at Louisiana State University report that the shelf life of good-quality raw shrimp and oysters given a dose of from 100 to 200 krads can be extended for 7 to 12 days for shrimp and for 6 to 7 days for oysters.*

An AEC contract has been held by researchers at Louisiana State University (LSU) since 1962 to investigate radiation treatment of shrimp and oysters. The program was terminated at the end of 1969. In the final report, the results of 8 years' research are summarized.

The program instituted at LSU in 1962 was designed to determine the feasibility of extending the storage life of shrimp and oysters by using low doses of gamma radiation to lower the initial load of microorganisms. Several factors had to be investigated: (1) optimum dose of radiation—largest reduction in bacteria with smallest change in the product, (2) organoleptic acceptability of irradiated products—tested by taste panels, (3) nutrient stability during irradiation and storage, (4) role of bacteria that survive irradiation, and (5) effects of transportation on irradiated products.

SHRIMP

First studies showed that doses of 50 to 100 krads extended storage life in ice (0°C) for 2 weeks beyond controls. The keeping quality after irradiation was dependent on quality before irradiation; irradiation did not improve quality—it only maintained good quality. Bacteriological tests showed that the total plate count decreased as the dose level increased. Chemical tests were used to ascertain the effect of radiation on the production of microbial metabolites. The amounts of ammonia nitrogen and trimethylamine nitrogen were considerably lower in the irradiated product; the *p*H value was also lower.

Doses between 100 and 250 krads were investigated with both raw and cooked shrimp. Irradiation at 150 krads gave a longer shelf life, but the irradiated cooked shrimp was not as acceptable as the irradiated raw shrimp. The recommendation at this point in the program was that shrimp be irradiated to 150 krads as soon after catch as possible in a raw, deheaded, unpeeled condition.

Organoleptic evaluations indicated that panelists preferred irradiated shrimp to nonirradiated shrimp when both were stored on ice for more than 15 days. All samples were analyzed bacteriologically before being presented to the panels; no pathogens were found on any of the shrimp presented.

One study investigated changes in flavor components after irradiation. Volatile fatty acids were isolated from irradiated and nonirradiated fresh shrimp and compared by gas–liquid chromatography. Acids found included formic, acetic, propionic, butyric, valeric, caproic, myristic, palmitic, stearic, arachidic, *N*-henhenic, and isohenhenic. Both samples contained the same acid fractions and their isomers; the concentration of C_{20} was lower and that of C_{22} was higher in the irradiated samples.

Carbonyl compounds present in both the irradiated and nonirradiated samples included acetaldehyde, propionaldehyde, isobutyraldehyde, *N*-butyraldehyde, 2-methyl-1-pentaldehyde, 2,4-pentadienal, 2,4-pentadione, 2-hexanal, 2-octanal, and citronellal. Acetone was present only in the nonirradiated samples. Amino compounds identified were trimethylamine, ammonia, methylamine, dimethylamine, ethylamine, propylamine, and butylamine. The irradiated samples had lower trimethylamine and ammonia and higher methylamine content than did nonirradiated samples.

Another study was conducted to identify bacteria that survive a dose of 100 krads in shrimp. Organisms identified were *Brevibacterium minutiferula, Gaffkya homari, Sarcina flava, Bacillus megaterium, Achromobacter eurydice, Bacillus firmus,* and *Bacillus pumilus.*

A dose of 150 to 200 krads was found to significantly reduce the degree and amount of melanosis (black spot) in brown shrimp. Irradiation indirectly inactivated the enzyme that caused melanosis, i.e., phenolase, probably by radiolysis of the water and oxygen which diffused through the skin joints between the segments. The radiolysis products

*Summary of USAEC Report ORO-676, February 1970.

may have inactivated the phenolase. However, irradiation of commercial shrimp after melanogenesis had begun accelerated the process. End products of the reaction sequence are competitive inhibitors of the reaction, and if radiation had destroyed the capacity of the end products to inhibit the reaction, melanogenesis would be accelerated.

The determination of "freshness" of shrimp was attempted by rapid measurement of physical or chemical properties that change with spoilage. Viscosity of shrimp homogenates was shown to be related to texture. Statistically correlated values obtained by viscosity measurement and by organoleptic evaluation showed that as the viscosity rose, the organoleptic score declined.

Transporting shrimp under conditions that maintain good quality has always been difficult. Even when shrimp leave the processing plant with low bacterial counts, free from black spot and in good condition, they sometimes arrive decomposed and otherwise unfit for human consumption. The apparent cause has been irresponsible shippers who fail to maintain proper refrigeration conditions. Also, refrigeration units sometimes fail, and shipments are sometimes misplaced.

Studies of shipments between Baton Rouge, La., and Gloucester, Mass., were conducted by LSU and the Bureau of Commercial Fisheries Technological Laboratory.* Organoleptic and bacteriological evaluations showed that 100 krads was the minimum dose that satisfactorily extended the keeping qualities of shrimp.

In the final year of the program, the bacteriological profile of frozen, headless, unshelled shrimp obtained along the Gulf Coast was studied. Samples were obtained and evaluated for total coliforms, fecal coliforms, and total plate count. Total plate count could not be directly correlated to coliform contamination. Total and fecal coliform tests are now receiving much more attention as measures of low-quality shrimp.

OYSTERS

Oysters were irradiated within 24 hr after being taken from the beds. Doses up to 300 krads were used, but 300 krads induced a light-yellow exudate that was detrimental to oyster appearance. Doses have since been limited to no more than 250 krads, which reduced the bacterial load 98%. Organoleptic evaluation showed that irradiated oysters were much more acceptable at the end of the storage period than were nonirradiated oysters.

Chemical analyses showed that ammonia nitrogen and trimethylamine nitrogen values were lower in irradiated oysters. Since these two substances are metabolic products of bacteria and since bacteria are markedly reduced by radiation, this result was logical.

As with the shrimp, several other studies were conducted to ascertain the feasibility of the irradiation process. Bacteria surviving a 100-krad dose were found to be *Pseudomonas erythra*, Genus *Flavobacterium*, Genus *Pseudomonas*, *Neisseria flavescene*, *Neisseria sicca*, *Paracolobacterium intermedium*, *Alcaligenes metalcaligenes*, *Achromobacter butyri*, *Bacillus laterospores*, and *Protoaminobacter alboflavus*. An intensive study was conducted of the effects of irradiation on the proteolytic mechanisms of these bacteria. Since proteolysis precedes spoilage, the determination of the role of radiation in affecting the bacteria's ability to degrade protein and thus produce undesirable metabolic products and alter nutrient value of oysters was considered extremely important. Results indicated that irradiation caused a reduction of proteolytic activity by all bacteria. Correlation coefficients showed a significant relationship between the decrease in proteolysis and the decrease in bacterial numbers after irradiation. The reduction could be due partly to alterations in the bacterial metabolic pathways of formation of products. Further studies conducted under private funds have, in fact, shown that specific bacterial enzyme systems are affected by radiation.

An investigation undertaken with the Alabama Department of Public Health on destruction of coliform organisms in oysters showed that at present many oysters taken from Gulf waters cannot pass standards for total and fecal coliform counts unless they are irradiated.

An assay of B-complex vitamins in irradiated oysters showed that thiamine, niacin, pyridoxine, biotin, and vitamin B_{12} all decreased after irradiation. Riboflavin, pantothenic acid, and folic acid all showed increases after treatment. A study of the stability of other nutrients showed the only one significantly affected to be crude protein. However, when these values were converted to true protein, the decrease was not statistically significant. Storage decreased the ash content. (Appreciable amounts of minerals could have been leached into the liquid medium from the oyster tissue during lengthy storage.)

*Now: Fishery Products Technological Laboratory, National Marine Fisheries Service, U. S. Department of Commerce.

PROGRAM CONCLUSIONS

Oysters and shrimp are costly, highly perishable food items; many thousands of dollars worth of these products spoil annually. Gamma radiation in the range 100 to 200 krads can be successfully used to extend the iced-storage life of shrimp for 7 to 12 days and of oysters for 6 to 7 days.

Shrimp and oysters to be irradiated must be of good quality. Irradiation does not improve quality; it maintains quality. More importantly, irradiation cannot be used as a substitute for correct handling. Irradiation, if used properly, can alleviate many of the existing spoilage problems of these two excessively perishable foods.

Section
IV
Isotopes and Radiation Technology

Process Radiation Development

Electron Curing of Coatings: State of the Art, 1970*

By Allan S. Hoffman†

Supplementary Keywords: *review, technical; bibliography; accelerator; coating; industry, plastics; polymerization; economics.*

Abstract: *The state of the art (42 references) of electron curing of coatings is surveyed and analyzed from the chemical, radiation, engineering, and economic viewpoints.*

Electron-beam curing of coatings—application of a thin coating of a viscous liquid mixture onto a substrate, followed by passage under the electron beam from an accelerator to solidify the coating in a matter of seconds—has become a commercial reality in the United States. Ford Motor Company licensed[1] its "Electrocure" process for wood substrates to Boise Cascade Corp. (although the Boise pilot facility is at present shut down). Ford is also developing coil coatings for aluminum siding and for automotive uses.[2] Others known to be very active in this field in the United States include PPG Industries, Inc. ("Selectron" process) and The O'Brien Corp. (South Bend, Ind.).[3]

In conventional coating techniques, coatings are dried in long ovens, often with the evolution of a solvent. Radiation curing has a number of advantages over conventional curing processes—for example, higher line speeds are possible, less plant space is needed, and solvent-free coatings are used, lessening solvent-recovery and pollution problems. The product contains no catalyst residues, and there is no heat to damage the substrate. Finally, there is more efficient use of power, and the accelerator, an on–off power source, requires little maintenance. Among the disadvantages of this process, which is most efficiently adapted to flat substrates, are the need for new paint compositions since conventional paints are not, in general, cured by irradiation. These new coating compositions are usually very viscous and create engineering problems of application onto substrates moving at high speeds. Inert atmospheres are generally needed for good surface curing, and evaporation of reactive components from the coating mixture must be minimized for good final coating properties and process economics.

Important applications for the products are in prefinished wood panels for both indoor and outdoor use, as coil coatings for cans and closures, in residential siding, in mobile homes, in appliances, and in automobiles. Wood panels are generally coated with a relatively thick coating (e.g., several mils) in a relatively slow-moving process (50 to 150 ft/min). Metal coils may receive only a 0.5-mil coating while moving at speeds up to 500 to 600 ft/min. A major goal at present is to achieve similar line speeds for a radiation-curing process. Future applications of radiation curing include the drying of printing inks and adhesives in general.

This review ties together the complex interactions between coating compositions, radiation-curing mechanisms, and accelerator characteristics. Economic considerations are discussed, but no attempt has been made to survey and analyze the patent literature, which is included in a recent publication.[4] Two recent reviews on this subject are cited.[5]

*This article is a condensation of a paper presented at the International Atomic Energy Agency Panel on Radiation Processing in Developing Countries, Seoul, Korea, September 1970, and at IAEA/Takasaki Regional Training Course in Radiation Processing, Tokyo, October 1970, and is being published in *Atomic Energy Review*.

†Professor in departments of Chemical Engineering and Bioengineering, University of Washington, and Visiting Fellow, Battelle Seattle Research Center, Seattle, Wash. 98105.

RADIATION CONSIDERATIONS

Since higher line speeds are a major advantage of radiation-curing processes, the radiation dose required for 100% cure must be delivered in very short times, i.e., at very high dose rates. Typical doses required for curing of coatings range between 1 and 10 Mrads, which are delivered by electron accelerators in a shorter time than by other radiation sources (Fig. 1).

For a total length of 1 ft exposed to the radiation beam in any one process line, the required dose rates range between 100 and 1000 Mrads/min for a line moving at 100 ft/min. Since most existing accelerators do not deliver much more than 100 to 200 Mrads/min (over a reasonably large area), both coatings that can be cured with very low doses and high-intensity beams extending over long line distances are needed.

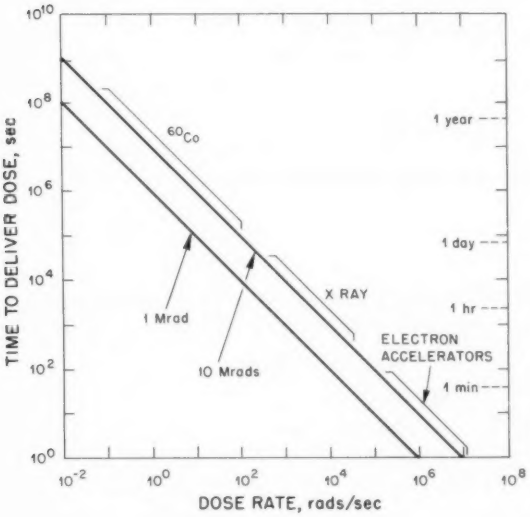


Fig. 1 Time required for different radiation sources to deliver a total dose of 1 or 10 Mrads.

The electron energies needed to cure coatings depend on the thickness and density of the accelerator window, the air gap, and the coating itself. As much as possible of the electron energy should be deposited uniformly through the coating, which may be done by adjusting the electron energy and the air gap (Fig. 2) for any particular process in which the thickness and density of the accelerator window and coating are constant.[6a,7] This was the procedure used in the Boise pilot plant, with a 300-kV power supply with two

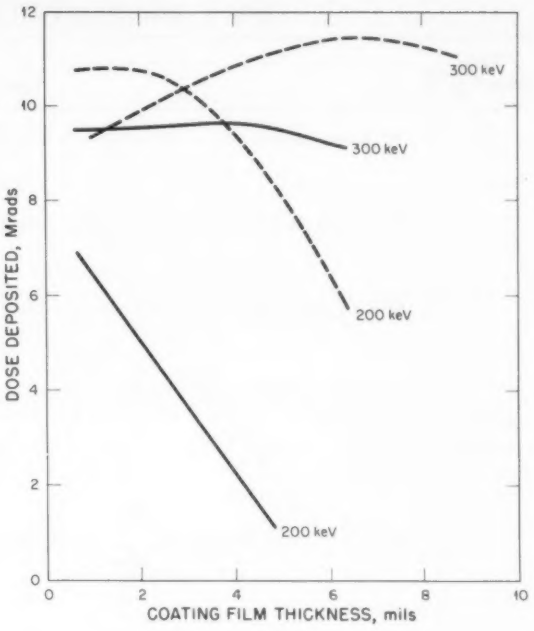


Fig. 2 Variation in electron dose with accelerator energy.[7] ——, 8-in. air gap; —, 2-in. air gap.

accelerator tubes, each capable of 15 kW output (50-mA currents). The tubes may be in series or parallel, depending on the panel width.

Most coatings of interest are between 10 and 200 μ thick (~0.4 to 8 mils), and electron energies of 25 to 150 keV are needed to penetrate such thicknesses. With the typical accelerator windows and air gaps encountered in practice, accelerator ratings of 150 to 600 kV are required.[6b]

CHEMICAL CONSIDERATIONS

When ionizing radiation is absorbed in organic matter, ions and excited molecules are produced but are rapidly converted to free radicals—the active chemical species that promotes the curing of coatings. With paints having high pigment contents, there may be ionic reactions. Efficient use of free radicals is obtained by promotion of chain reactions, such as polymerization, in which each free radical propagates over many reaction steps before it is terminated by reacting with another free radical. The high-intensity electron beams used for curing of coatings produce high local concentrations of free radicals, and propagation is emphasized over termination reactions by

Table 1 Examples of Polyunsaturated Monomers and Polymers

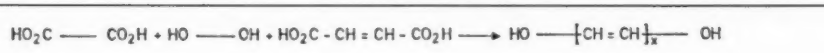
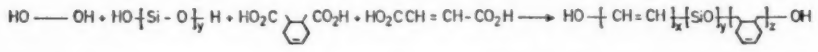
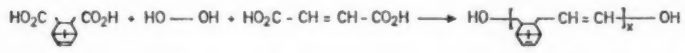
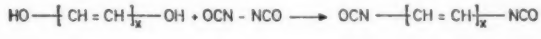
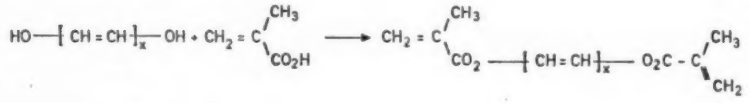
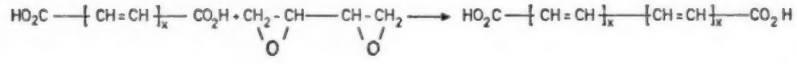
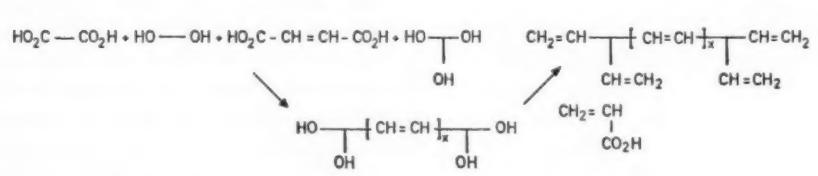
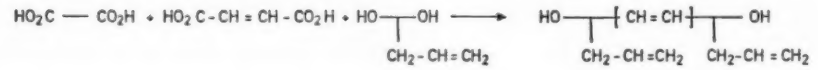
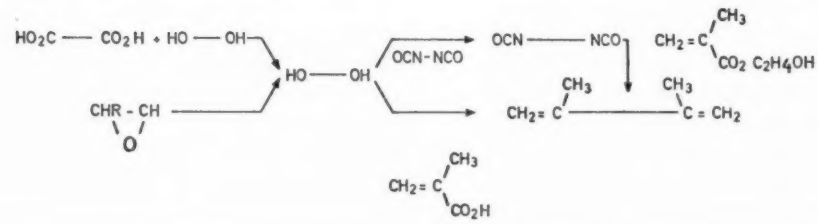
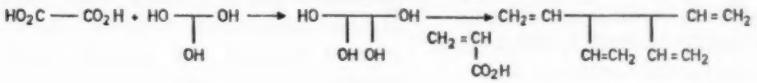
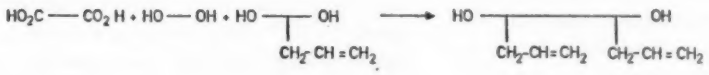
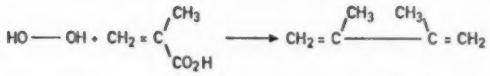
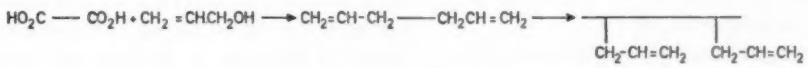
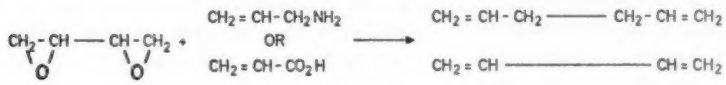
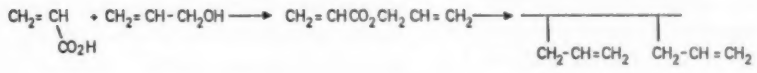
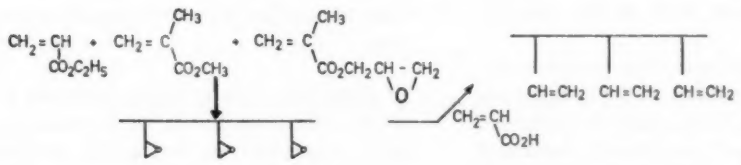
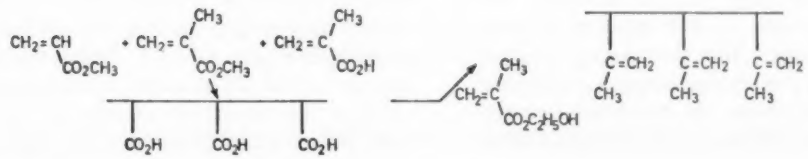
Type (from Fig. 3)	Chemistry	Ref.
1		Common polyester
		9
		10
		10
2		11
3		12
4		Variation on 5*b*,11
5		5*b*
6		13 14 11

Table 1 (Continued)

Type (from Fig. 3)	Chemistry	Ref.
7		5*b*
8		Variation of 5*b*
9–12		Commercially available di-, tri-, tetraacrylates and methacrylates
		15
		16 17
13, 14		Allyl acrylate
15		Diallyl fumarate
16		18
		19

retarding the mobility of the growing polymer chains such that reaction between any two such chains is less likely than between a mobile monomer molecule and a free-radical chain end—the so-called "gel effect."

Consequently, coatings are used which not only are initially viscous but also rapidly increase in viscosity (due to free-radical polymerization reactions) as the radiation is absorbed. The new coating compositions used are mixtures of monomers and polyunsaturated monomers and polymers (Table 1). Condensation, ring opening, and addition polymerization may all be involved in synthesizing the polyunsaturated components. The molecular weight, degree, and type of unsaturation are the major compositional variables of the polymer component. The final coating is the result of free-radical copolymerization reactions between monomer and polymer double bonds, yielding a cross-linked, insoluble, and infusible gel whose properties depend on the compositions of the various components and the cross-link density.

The degree of curing of a coating may be measured by the degree of gel formation—i.e., the percentage of gel formed per megarad of dose. Thus the degree of curing is affected by the composition and concentration of the monomers and polymers, the frequency and type of unsaturation of the polyunsaturated monomers and polymers, and the molecular weight of the polymers. In general, a higher frequency of unsaturation and higher molecular weight of the polymer should both increase the degree of gelation for any one monomer(s)/polymer ratio in the coating mixture. However, if the frequency of unsaturation along the polymer backbone is too high, steric hindrances will impede the reaction of many of the double bonds as the polymer chains enter into the gel phase (this also leads to aging problems with the final coating). Furthermore, higher molecular-weight polymers are harder to dissolve and more viscous in solution, and thus there will be an upper limit to the polymer molecular weight.

Economic considerations also play an important role in the selection and synthesis of the components of a coating. For example, if very reactive monomers are used—especially the polyunsaturated monomers (e.g., di- and triacrylates)—the degree of unsaturation of the polymer component may be decreased, and possibly even commercially available saturated polymer backbones may be used.[8] Thus the coating composition will represent a compromise between component selection, polymer synthesis and dissolution, coating application and curing efficiency, and the final coating properties.

CURING MECHANISM

A number of studies have been published on the radiation gelation of mixtures of monounsaturated and polyunsaturated compounds. Early workers[20-23] irradiated unsaturated polyester–monomer (usually styrene) mixtures and generally made distinctions between catalytic- and radiation-curing procedures. More recently, new polyunsaturated compounds have been synthesized (Table 1), and radiation-curing mechanisms have been more intensively investigated.[10,24-30] The curing mechanism is affected by the total dose and dose rate; monomer concentration and composition; polymer reactivity, molecular weight, and composition; and the type of double bond.

Effect of Dose and Dose Rate

Dose. In general, the greater the dose the greater the extent of gelation (Fig. 4). (Data characterizing the polyester backbones shown in Fig. 4 are presented in Table 2.) However, a limiting gel content may be observed with increasing dose in a system where network chains are solubilized due to radiation degradation at the same rate as soluble chains are incorporated into the network. Charlesby and Wycherley[22] also suggested a limiting curing level in styrene–unsaturated polyester mixtures due to the immobilization (or trapping) of the growing chains as gel is formed and monomer is depleted. (They did, however, observe posteffects due to these radicals.) On the other hand, Hoffman and Smith[26] noted an increase in gel content from 38 to 78% when they reirradiated (4 Mrads) a partially cured specimen, which had originally received a 4-Mrad dose and from which monomer had been removed after the first irradiation by evacuation at room temperature. They ascribed this effect to an increase in termination reactions of trapped radicals, formed during the first irradiation, with radicals formed nearby during the second irradiation.

Dose Rate. The radiation dose rate is a relatively poorly understood parameter, especially in view of its great importance in the curing mechanism. Some machines emit pulses of electrons which are magnetically scanned at high frequency across the beam window and along in the machine direction, tracing an accordionlike path, ⌐¬⌐¬. Other machines emit a constant stream of electrons from a linear filament, which is then spread out over an area by a magnetic field. Most machines have metallic windows, but at least one does not.

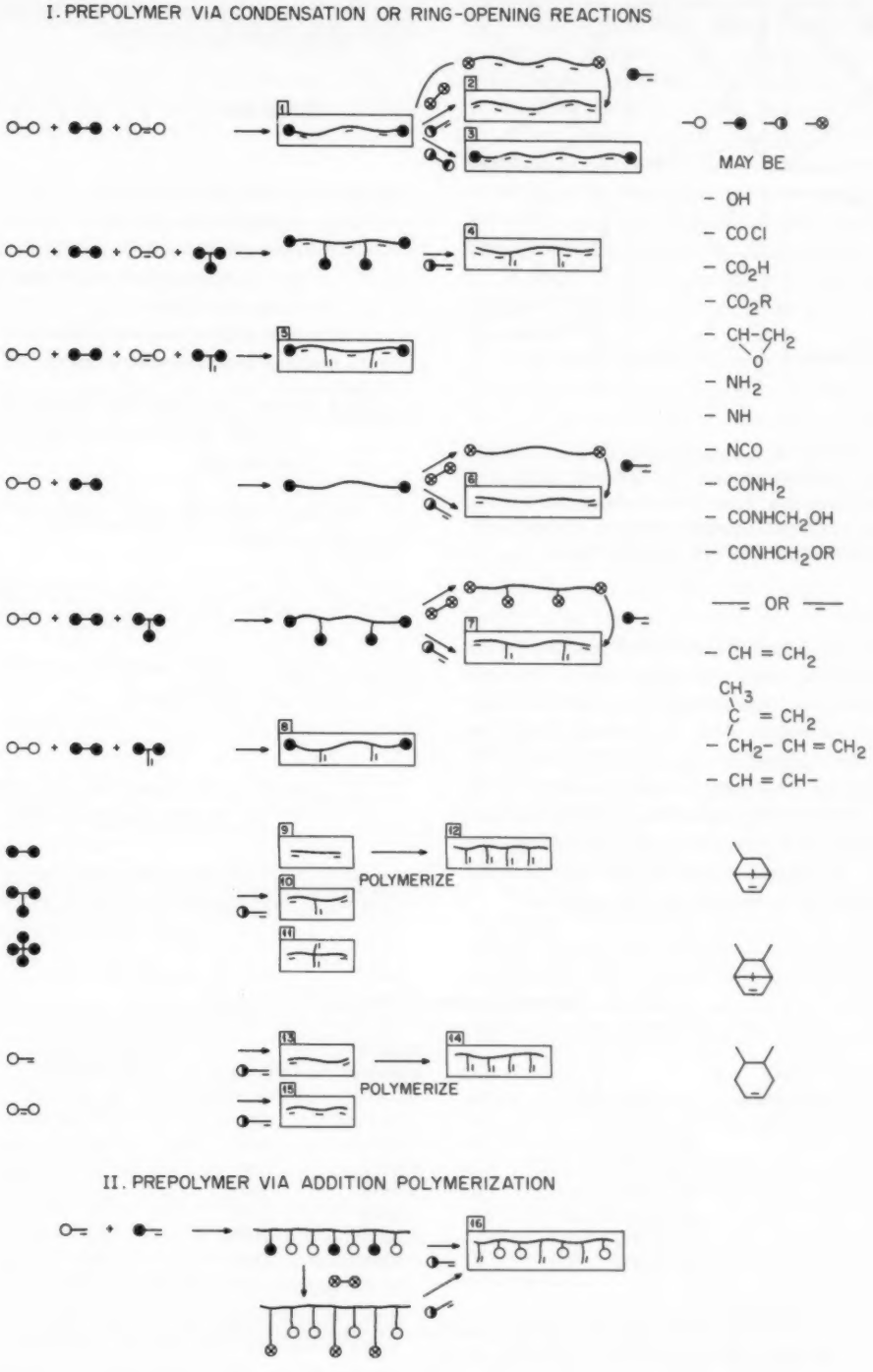


Fig. 3 Schematic preparation of polyunsaturated monomers and polymers for radiation-curable coatings.

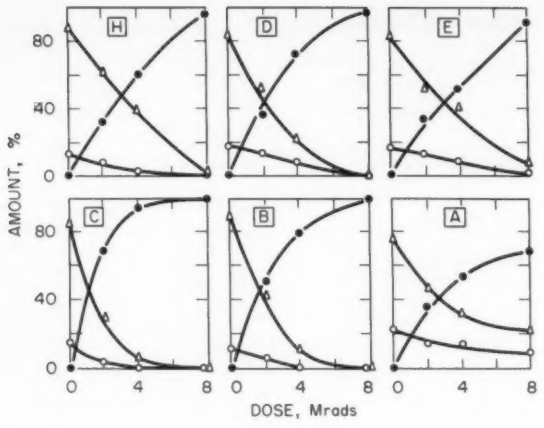


Fig. 4 Effect of dose on the formation of gel from (soluble) polyester and (volatile) styrene for different unsaturated polyester backbones (see Table 2 for meaning of letters). Initial styrene contents[27] ranged between 11 and 23%. ●, gel; △, soluble material; ○, volatile material (styrene).

Although the gelation kinetics are sensitive to the instantaneous, local dose rate (especially in the early stages of cure), the time-average dose rate is usually measured or estimated. This time-average dose rate depends on the original energy of the electron, the window thickness, composition and scanned area, the distance between the window and the coated substrate, the composition and pressure of the gas between the window and the coated substrate, and the thickness and composition of the coating and the substrate.

The time-average dose rate through the thickness of the coating films may be written

$$\text{Dose rate} = \frac{1}{\rho x_0} \int_0^{x_0} \frac{i}{WL} \left(\frac{dE}{dx}\right)_i dx$$

where ρ = coating density, g/cm^3
x_0 = coating thickness, cm
i = time-average number of electrons arriving at the coating surface, each having an average energy E, electrons/sec
W = scan width (transverse direction)
L = scan length (machine direction)
$\left(\frac{dE}{dx}\right)_i$ = linear rate of energy transfer in the coating for each electron of average energy E, ergs/cm-electron

The dose delivered to a substrate moving at a velocity v is then

$$\text{Dose} = \frac{L}{v} \times (\text{dose rate}) = \frac{1}{v\rho x_0 W} \int_0^{x_0} i\left(\frac{dE}{dx}\right) dx$$

$$\text{Dose} \approx \frac{\text{const.}}{v(\rho x_0)} \quad \text{(for a particular set of irradiation conditions)}$$

or

$$\approx \frac{(\text{const.}')}{v} \quad \text{(for a particular set of irradiation and coating conditions)}$$

Early work of Ballantine and Manowitz[21] and of Charlesby and coworkers[32] with gamma radiation

Table 2 Characterization of Polyester Backbones*

Resin designation	Composition†	Acid No.	Intrinsic viscosity $[\eta]$, dl/g	Estimated mol. wt. ($\bar{M}_n$)‡	% gel formed with 8 Mrads in air
C	IP/MA/PG = 1/1/2	15.6	0.087§	2400	60
H	PA/MA/PG = 1/1/2	47.2	0.041§	800	5
D	IP/FA/DEG = 2/1/3	16	0.083¶	2300	58
E	IP/FA/DEG = 2/1/3	25	0.066¶	1700	48
A	IP/MA/PG = 3/1/4	11	0.087§	2400	21
B	IP/MA/PG = 2/1/3	15.1	0.079§	2100	35

*From Ref. 27.

†IP = isophthalic acid; PA = phthalic anhydride; MA = maleic anhydride; FA = fumaric acid; PG = propylene glycol; DEG = diethylene glycol.

‡Calculated[31] from $[\eta] = (4.8 \times 10^{-4})\bar{M}_n^{0.67}$, determined for a polyester resin of composition IP/MA/PG = 1/2/3 in chloroform at 30°C.

§Measured in benzene, 23°C.

¶Measured in chloroform, 23°C.

showed that the dose required for gelation varied with the square root of the intensity. Charlesby and Wycherley,[22] using electron irradiation, emphasized the importance of primary radical termination at the higher intensities, leading to shorter kinetic chain lengths.

More recently, Burlant and Hinsch[25] studied the effect of electron dose rate on the rate of disappearance of polyester double bonds in 65% unsaturated polyester–35% styrene solutions. They showed a linear increase in $d\alpha_t/dt$ with increasing dose rate (where α_t is the fraction of initial unsaturation that has reacted at time t) up to about 20 Mrads/min. At higher rates, $d\alpha_t/dt$ leveled out and then decreased slightly up to 85.8 Mrads/min (Fig. 5). They used a 300-kV High

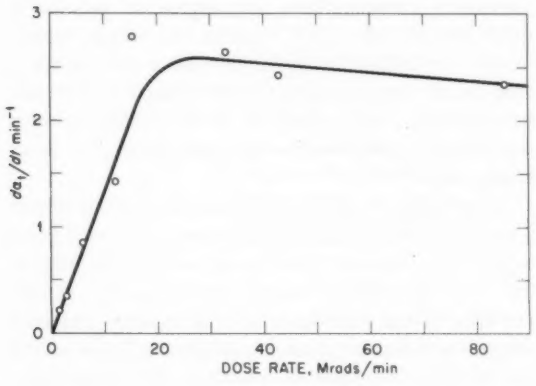


Fig. 5 Rate of disappearance[25] of polyester unsaturation as a function of dose rate, where α_t is the fraction of initial unsaturation that has reacted at time t.

Voltage ICT accelerator and (presumably) scanned the electron beam across the sample, which was exposed to the beam by rotating over the sample a disk containing a small slit. They concluded that the gelation, which was much more rapid than expected from normal free-radical kinetics, was initiated by a "hot radical" in isolated volume elements (electron tracks) up to 20 Mrads/min, beyond which the electron tracks overlapped and a very short, limiting kinetic chain length was arrived at in a more or less homogeneous reaction system. Thus it is conceivable that the leveling out of $d\alpha_t/dt$ could be due to the continual increase, with dose rate, in the local concentration of small primary radical fragments, such as H•, which can escape the track at low dose rates but which eventually, when the tracks overlap, predominantly recombine with other radicals (e.g., growing chains). This would be especially favored in a viscous or glassy matrix. Hoffman and coworkers[27] noted a similar upper limit to the initial efficiency of gelation at ~10 Mrads/min for 70% unsaturated polyester–30% styrene systems (Fig. 6).

Three points may be emphasized from these last two studies:

1. Scanning the beam and/or rotating a shutter apparently makes no difference in the dose-rate effects; only time-average dose rates are important.

2. Most of the data pertain to rates of gel formation below the region of very high gel contents—75% and more.

3. Dose-rate limitations might not be encountered or might be displaced to higher intensities (at any dose) or lower doses (at any intensity) in other than the systems unsaturated polyester–styrene compositions e.g., those shown in Table 1 or Fig. 3.

Davison and Greenwood[33] analyzed the dose-to-cure requirements for a styrene–unsaturated polyester system with delivery of the dose in many small "pulses"—i.e., multiple passes under a steady-beam current, similar in principle to the rotating-shutter device used by Hoffman et al.[27]

The number of passes varied between 1 and 50, with conveyor speeds between 0.1 and 3 m/sec; the length of the beam along the machine direction was either 0.02 or 0.15 m. All these conditions yielded time-average dose rates between 10 and 500 Mrads/sec. They arrived at a general relation wherein the dose to cure is inversely proportional to the number of passes raised to a power between 0 and 1.5.

This suggests that, for any time-average dose rate, increasing the scanning frequency of a steady beam would increase the degree of gelation. However, this conclusion may pertain only to systems where the radicals have time to propagate and terminate before the next pulse arrives—i.e., at low gel contents or at

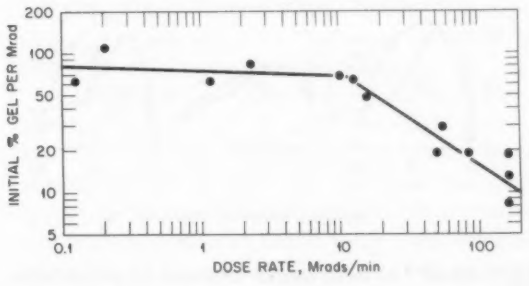


Fig. 6 Efficiency[27] of initial gelation reactions as a function of dose rate for polyester C (see Table 2) mixed with 30% styrene.

relatively low dose rates. As the dose, pulse, and/or frequency of pulsing or scanning increase, the time-average dose rate increases, and eventually we would expect to arrive at the limiting levels noted for the polyester–styrene system by Burlant and Hinsch[25] and Hoffman and coworkers.[27]

From still another viewpoint, Hoffman and Smith[26] found that, with styrene–polyester mixtures, if the total dose absorbed from a pulsed, scanned beam is fractionated into several passes (each at the same time-average dose rate of 120 Mrads/min), the gelation efficiency is greater than if the dose is absorbed in one pass. Pietsch[28] and Blin and Gaussens[30] confirmed this observation for the styrene–polyester system.

It is probable that, with the higher dose rates, rigid gel will be generated so rapidly that many growing chains will be trapped or immobilized. (This can lead to a posteffect,[26,32] as mentioned above, and a continued, gradual increase in hardness of the coating.[28]) This probability, along with the total of the observations made on dose-rate effects, suggests that the coating system may be dose-rate sensitive only as long as the radicals formed are mobile enough to propagate and terminate between pulses. If the pulse rate (or time-average dose rate) is very high or if the radiation sensitivity is high enough that a rigid network is rapidly formed at lower doses, we would expect the further cure of the coating to be dose-rate insensitive.

Finally, it is possible that the maximum in gel content with monomer content (e.g., Fig. 7*a*) may shift with dose rate, based on extrapolation of data obtained with ^{60}Co showing a minimum in the dose at the gel point for unsaturated polyester–styrene mixtures containing between 80 and 90% styrene.[34]

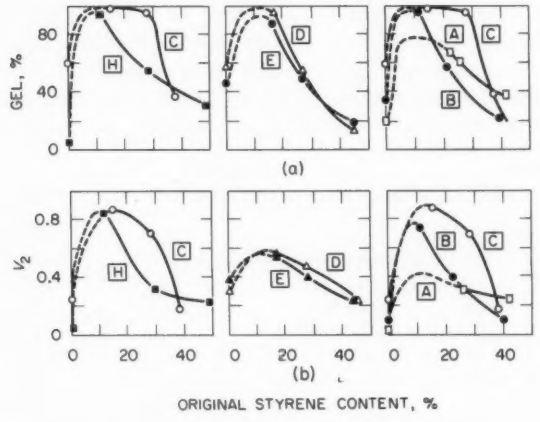


Fig. 7 Effect[27] of initial styrene content on (*a*) gel formation in styrene–polyester mixtures and (*b*) volume fraction of polymer in the 2-butanone swollen gel as a function of initial styrene content (Table 2 identifies the backbones). Dose = 8 Mrads.

Effect of Monomer Concentration

When unsaturated polymers are irradiated in the absence of monomer, gelation occurs due to reactions between the macroradicals formed.[26,32,35,36] Charlesby and coworkers, studying the gelation of polyesters in the absence[35] and presence[22] of styrene monomer, concluded that pure polyesters exhibit a gel reaction with a much shorter chain length than when styrene is present and apparently terminate via a monomolecular mechanism, as opposed to the bimolecular termination step expected with the styrene-containing systems. Thus the degree of gelation is much greater when the relatively immobile macroradicals are bridged by mobile monomer molecules in a free-radical copolymerization chain reaction. This will be especially true if a fraction of the mobile-monomer component is polyunsaturated monomer (e.g., a di- or triacrylate).[5b,30]

Eventually, however, as more and more monomer is added to the unsaturated polymer, two new factors begin to predominate. The first is a reduced viscosity in the coating mixture, which should permit greater mobility of the macroradicals, and thus an increased rate of bimolecular chain termination relative to the rate of chain propagation. This should be particularly true for high-intensity radiation, where the local free-radical concentrations will be high. The overall result is a diminution of the gel effect and a decreased efficiency of gelation.

The second factor is the decreased concentration of polymer unsaturation (or increased concentration of monomer molecules). This may also cause a decrease in curing efficiency since the final product at 100% conversion should now be a mixture of monomer-cross-linked polymer gel plus homopolymer. Since the efficiency of homopolymerization is usually low at high intensities, the viscosity does not rise as fast with dose as it did at lower monomer concentrations, and the gel effect once again is diminished. Both these factors lead to decreased gelation efficiency as monomer concentration increases. Eventually, as even more monomer is added, the viscosity is sufficiently decreased, and the polyunsaturated molecules are sufficiently diluted that very little gel will form at reasonable dose levels.

Thus there is a maximum gel formation as a function of monomer concentration at any dose, as

confirmed by Hoffman and coworkers[26,27] (Fig. 7*a*). Blin and Gaussens[30] also confirmed these trends.

Effect of Monomer Composition

Early work of Ballantine and Manowitz[21] with gamma radiation showed that styrene had a greater reactivity with the maleate or fumarate group on unsaturated polyester molecules than did other more reactive monomers such as vinyl acetate and methyl methacrylate. Hoffman and Smith[26] also found that polyunsaturated esters form gels more efficiently with styrene than with ethyl acrylate, which is still more efficient than methyl methacrylate. They suggested that in the case of methyl methacrylate, in addition to its lower reactivity with maleate bonds, the growing chain ends should terminate mainly by disproportionation, and, once formed, these chains may be subsequently scissioned by the radiation. However, when 50–50 monomer mixtures of styrene–ethyl acrylate or styrene–methyl methacrylate were mixed with the same unsaturated polyester resin (75% polyester, 12.5% of each monomer), the mixture was cured almost as efficiently as when only styrene monomer was used. These general trends have recently been confirmed by Blin and Gaussens.[30]

Pietsch[28] found that styrene was also more efficient in cross-linking unsaturated polyester resins than ring-substituted styrenes, acrylates, or even dimethacrylates.

Miranda and Huemmer[5b] showed that, in the absence of unsaturated polymer, only a few monomers were sensitive to high-intensity electron irradiation. Table 3 summarizes their results for monomers that displayed some reaction to the radiation.

From these results we would expect that other mono-, di-, and triacrylates would also be quite sensitive to radiation. Acrylic acid is also known to polymerize under electron irradiation. All these monomers should form gel efficiently when mixed with unsaturated polymers in the proper proportion.

Blin and Gaussens[30] studied the curing of different monomers mixed with four types of unsaturated polymers. Their data agreed with most of the general conclusions reached with unsaturated polyesters by Hoffman and Smith, and, in addition, they showed that the gelation efficiency of vinyl acetate was greater than that of methyl acrylate for 80% polyester–20% monomer mixtures.

Table 3 Monomers Sensitive to High-Intensity Radiation

Monomer	Observed effect	
	In nitrogen	In air
Trimethylolpropane triacrylate	Good cure, tack free	Good cure, tack free
Trimethylolpropane trimethacrylate	Cured, brittle	Cured, oily surface
1,3-butylene dimethacrylate	Cured, oily surface	No cure
2-hydroxyethyl acrylate	Rubbery product	Rubbery product
Butyl acrylate	Tacky rubbery product	Oily product
2-hydroxyethyl methacrylate	Jellylike fluid	No cure

Effect of Unsaturated Polymer Reactivity, Molecular Weight, and Composition

It is to be expected that at any one dose and monomer concentration, the greater the molecular weight and frequency of unsaturation along the polymer chain, the greater should be the efficiency of gel formation. Charlesby and Wycherley[22] originally confirmed the effect of frequency of unsaturation for cobalt irradiation. This was verified for electron irradiation by Hoffman and coworkers,[26,27] who studied the gelation of a series of different unsaturated polyester resins mixed with sytrene monomer (Table 2). They noted the following effects on gel formation as the styrene content increased:

1. In the absence of monomer, gelation efficiency increases for both greater molecular weight (C vs. H and D vs. E—see Table 2) and increased polymer unsaturation (C vs. B vs. A). The molecular weight appears to be somewhat more important than unsaturation frequency, all other factors being equal. There also appears to be a greater reactivity toward gel formation in chains of equal molecular weight and double-bond frequency when diethylene glycol (DEG) is substituted for propylene glycol (PG) in resin D vs. B. This may be due to the greater radiation sensitivity of DEG vs. PG

and/or to the greater flexibility of the polyester chains containing DEG.

Omel'chenko and coworkers[10] also showed that unsaturated polyesters containing di- and triethylene glycols were more reactive in forming a gel with styrene (under ^{60}Co gamma irradiation) than was ethylene glycol. Their data also indicated that unsaturated polyesters synthesized with the longer aliphatic dibasic acids (e.g., sebacic) formed gel more efficiently than did the shorter aliphatic or aromatic dibasic acids. In general, we expect that any aromatic groups present on the polymer, monomer, or inhibitor molecules will increase the dose required for 100% conversion due to the protective effect conferred by these groups.

2. In the region of the maximum in curves of gel content vs. styrene concentration (Fig. 7*a*), the frequency of unsaturation along the backbone appears to be more important than the molecular weight, although both play an important role in the gelation mechanism. Since this is the region where copolymerization reactions between monomer and polymer predominate, it is to be expected that polymer unsaturation frequency will be a very significant factor.

3. As styrene contents increase beyond the maximum, we observe a crossover of curves, which indicates a reversal in the order of reactivities toward gel formation in these high-styrene systems (e.g., in Fig. 5*a*, H > C, E > D, and A > B > C). Hoffman and coworkers[27] suggested that this was due to the different compatibilities of the polyester chains with styrene, so that the shorter chains or the least unsaturated chains (with a greater aromatic content if isophthalic acid is substituted for maleic anhydride) would be more compatible with styrene and would therefore react more efficiently with it as the polyester chains become more and more diluted by the monomer. Indeed, gel-swelling measurements in 2-butanone indicated that the gels formed at high-styrene contents (>30%) swelled to extents similar to those of gels formed at low-styrene contents (<10%) (Fig. 7*b*). This suggests that the gel formed at high-styrene contents may be forming in regions of incipient phase separation where the styrene/polyester ratio is much lower than the average in the solution. The most tightly crosslinked gels were those in which the polyester chains reacted most efficiently, since the same crossovers were noted with both the swelling data and the gel data as a function of styrene content.

Nordstrom and Hinsch[18] also investigated the effect of unsaturation content in an acrylic polymer backbone (Table 1) dissolved in (50%) methyl methacrylate in which unsaturation levels varied between 0.4 and 3.0 moles of double bonds per 1000 molecular weight. They concluded that the optimum range for useful coatings is between 0.5 and 1.75 moles of pendant acrylate double bonds per 1000 molecular weight.

The molecular requirements for the most efficient radiation-curable unsaturated polymer–monomer solutions may be summarized broadly as

Method of polymer synthesis	Polymer molecular weight	Double bonds per polymer molecule	% monomer mixed with polymer
Condensation (e.g., polyester)	1,000– 3,000	1–6	10–25
Addition (e.g., polyacrylics)	10,000–50,000	5–25	15–50

Effect of Double-Bond Type

As shown in Fig. 3, a variety of double bonds may be attached along the polymer backbone, at the ends of the polymer molecule, or pendant to it, and these chains may be dissolved in different monomers containing different double bonds. Obviously, some combinations of backbone and monomer unsaturation will be more reactive than others. In fact, it is entirely conceivable that, since some of these combinations are more reactive than others, they will not display the same dose-rate sensitivity, especially in the early stages of cure when the chains are most mobile. Rapid viscosity buildup is a prerequisite to high curing efficiency.

Although no systematic comparison has been made between the various double bonds and their location in the solution, two generalities may be made:

1. For chain end, pendant, or monomer unsaturation, the expected order of decreasing reactivity is

$$-CH{=}CH_2 > -\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2 > -CH_2{-}CH{=}CH_2$$

2. Internal double bonds, –CH=CH–, should not be so reactive as chain-end double bonds, which themselves should be sterically more accessible than pendant double bonds. (An exception is the exceptionally reactive maleate or fumarate–styrene pair.)

It is also now known where the internal, cyclic double bonds would fit into these orders of reactivity. Norbornenyl double bonds have been shown to cause rapid cross-linkage when polymers containing them are exposed to radiation.[37]

ENGINEERING CONSIDERATIONS

Surface Cure

Free-radical scavengers in the coating mixture will retard the copolymerization reactions until these compounds are exhausted. For most inhibitor levels used, and even for air dissolved in the coating mixture, this can require as much as 1 Mrad or more before the gelation reactions can proceed efficiently in the bulk of the coating.

Air may always be removed from the mixture by degassing the monomer before dissolving the polymer, after which the solution may be stored under an inert gas, such as nitrogen. If the pressure of the inert gas is increased, the dissolved gas may produce a protective blanket over the coating if irradiation follows immediately after application of the coating on a substrate. If, however, oxygen is present in the atmosphere above a coating during irradiation, the surface cure will be inhibited. It is not likely that oxygen molecules will penetrate much beyond the surface at the high intensities used. This can lead to a tacky or only partially cross-linked surface layer, which may not have a good appearance and which will age rapidly upon exposure to the elements. Addition of paraffin wax to the coating mixture, as is done in thermal peroxide curing of coatings, cannot be used here with high-speed lines because there is not enough time for the wax to diffuse to the surface of the coating before it is irradiated. Therefore radiation curing of coatings is generally run in an inert (nonoxidizing) atmosphere. For example, Boise Cascade Corp. maintained a reducing atmosphere by incomplete combustion of desulfurized natural gas.[7] Some inert-gas atmospheres may be more effective than others in permitting good surface cures, and cost will play an important role in the choice of atmosphere.

It is possible that, at high intensities with very reactive coating mixtures, the peroxides formed on the surface due to reactions of the free radicals with O_2 or O_3 will be scissioned by the radiation and/or be decomposed thermally as the polymerization exotherm and radiation energy input raise the coating temperature. This can lessen the inhibiting effect of oxygen.

Evaporation Losses

Even though the polymerization exotherm is much more under control with radiation curing than with peroxide curing,[38] and, in fact, whether or not there is any temperature rise of the coating, there can be significant evaporation losses of volatile monomer because of the large coating surface area exposed before the monomer is consumed in copolymerization reactions. Evaporation of monomer may be very critical for two major reasons: (1) control of the gelation reaction, and thus of final-product properties, may be difficult since the curing mechanism is so sensitive to monomer content, and (2) a monomer-recovery system may be needed—a costly item, which eliminates one of the major advantages of using radiation. Thus monomer evaporation must be controlled and kept to a minimum by using low-volatility monomers and by covering the coating or enclosing the coating system until it is cured.

Application

Most coating systems developed for radiation curing are quite viscous, and, since many end uses require application at high speeds, there have been significant engineering problems in the rapid application of thin, smooth, bubble-free coatings. Vanderbie and coworkers[7] concluded that curtain coating is preferable at high speeds, while roll coating and spray application may be used at lower speeds and/or lower viscosities. Reverse roller coating may be the preferred technique for an installation having maximum versatility of operation. The advantages and disadvantages of the application techniques may be summarized as follows:

Curtain coating: Yields best appearance, especially at high speeds (>300 ft/min), but requires large space and may entrain bubbles, and coating solutions must readily form a thin curtain.

Roll coating: Requires smallest space, but a ribbed pattern may appear, especially with higher viscosities or higher speeds, and foreign particles cause streaks.

Spray coating: Difficult to apply with higher viscosities or higher speeds, and orange-peel pattern is possible.

The addition of pigments to the coating mixture can significantly increase the viscosity, although the dose required to cure is not greatly affected.[18]

If greater "build" is required, successive application and irradiation cycles may be used, although good adhesion between the different coats may be difficult to achieve. Ideally, we would want to apply a relatively

low-viscosity coating in one coat, expose it first to a low time-average dose-rate electron beam to raise the viscosity as rapidly and efficiently as possible in the initial dose-rate-sensitive curing region and then irradiate with a high time-average dose-rate beam to complete the cure in the increasingly rigid gel network where the mechanism has become dose-rate-insensitive.

catalyst) costs to be minor. He considered only the quantitative aspects and did not include an economic evaluation of differences in product quality. However, his results indicate that electron curing becomes more advantageous over chemical methods as the coating thickness and/or production rate increases. Trageser[41] agrees (Fig. 8), and Morganstern[42] has concluded that

Table 4 Cost Comparison of Irradiation and Catalytic Curing[41]

Coating thickness, mm	Production rate, m^2/hr	% of total cost					
		Hard-board	Coat-ing	Chemical curing*	Hard-board	Coat-ing	Irradiation curing
0.1	550	88.1	10.7	1.2	87.9	10.6	1.5
0.4	1100	62.8	35.9	1.3	60.4	34.4	5.2
0.6	2200	52.0	47.1	0.9	49.0	44.5	6.5

*Using 1.5% cyclohexanone peroxide + 0.05% cobalt naphthenate. No capital costs for equipment are included.

Aging

For the best aging characteristics, acrylic or other nonaromatic monomers and polymers are favored over styrene or polymer systems containing aromatic groups. It is also important that the double bonds in the coating be as completely reacted as possible since they are labile sites for oxidation (aging). The surface should also be especially well-cured since aging reactions are most easily initiated there. The polymer coating should also adhere well to the substrate. In the case of metal substrates, certain groups—e.g., $-CO_2H$ and $-\underset{\diagdown\,\diagup\ \ }{\overset{\ \ \diagdown\,\diagup}{CH-CH_2}}$ (O) —may enhance this adhesion by enhancing wetting. Shrinkage will occur during the curing, and it is important that the polymer gel formed should still wet the substrate.

Better weather resistance has been noted for radiation-cured styrene–polyester coatings than for chemically cured coatings.[39]

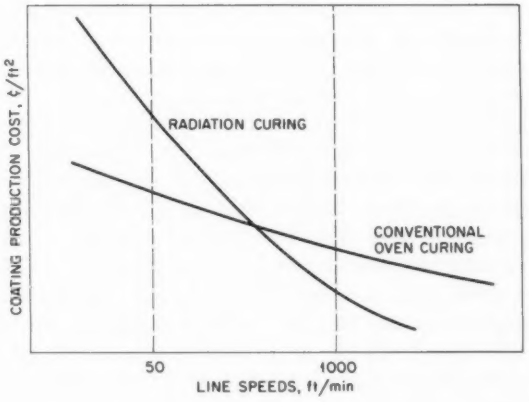


Fig. 8 Effect of line speeds on production costs for radiation and conventional oven-curing processes. (Schematic plot from Ref. 42.)

ECONOMIC CONSIDERATIONS

It is generally agreed that the major operating costs in the radiation curing of coatings are the costs of the coatings themselves (and the substrates), but this is also true for chemical curing or thermal drying of other systems. Rotkirch,[40] in a detailed analysis (Table 4) of the economics of coating of fiberboard panels with unsaturated polyester–styrene mixtures using either radiation or chemical curing, found radiation (or the operating cost of a radiation-coil-coating process running at line speeds of 200 ft/min may be less than half the costs involved in the conventional oven-curing process.

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Radiation-Initiated Emulsion Polymerization: Pilot-Plant Operation and Economic Feasibility Study*

By R. S. Allen, J. A. Ransohoff, and D. G. Woodard

(Summarized by R. E. Greene)

Supplementary Keywords: *polymerization; emulsion; industry, plastics; source, gamma; economics; pilot-plant scale; plant scale;* ^{60}Co.

Abstract: *Vinyl acetate–butyl acrylate copolymer latex produced on a pilot-plant scale by radiation-initiated emulsion polymerization was shown to be of commercial quality. The economics of large-size plants producing latexes by conventional and radiation-catalyzed processes are compared. This is a summary of USAEC Report ORO-673.*

Neutron Products, Inc., under contract to the USAEC Division of Isotopes Development, used ^{60}Co radiation to produce a vinyl acetate–butyl acrylate copolymer latex by emulsion polymerization on a pilot-plant scale. The plant used is representative of the type of system that would be constructed for a commercial radiation process. Polymerization by this method presents interesting possibilities for the production of latexes for the paint industry, which has annual sales of about $\$2.5 \times 10^9$.

PILOT PLANT

In the pilot plant the main reactor volume and all controls are located in a radiation-free area. The reaction mixture is continuously circulated through a zone of high radiation from ^{60}Co, where the initiating species are created and where most of the polymerization occurs. The plant is constructed of materials and components that would be used in a commercial plant and is of a size such that scale-up to commercial operation involves a modest extrapolation. Latex was produced in the plant by polymerization of monomer added in three ways—in batches, at a given rate until a specified quantity was delivered, and continuously. All materials used in the formulation of the experimental latexes were of commercial grade; there was no

*Summary of USAEC Report ORO-673, Neutron Products, Inc., October 1969. (Received at the Isotopes Information Center, Oak Ridge National Laboratory, January 1971.)

purification of materials prior to reaction; and a nonproprietary formulation was used extensively.

Latexes produced by radiation catalysis and paints made from the latexes were evaluated by several commercial firms and by an independent testing laboratory. Although latex properties varied somewhat from sample to sample, the paint from the latex was of commercial quality and had enamel holdout* superior to that of paint produced from high-grade commercial latexes made by conventional means. Although the work performed was not extensive enough to ensure that this property improvement is readily reproducible, it is likely that the improved enamel holdout does result from the higher polymer molecular weight obtained by the use of radiation initiation. In a practical test, several gallons were used to paint the cinder-block walls of six offices; paint performance appears highly satisfactory.

Operation of the pilot plant and evaluation of the product established that radiation-catalyzed latex with commercially acceptable properties can be produced in commercially feasible equipment.

The work did not result in the definition of a completely satisfactory commercial process because two process-development problems—the reduction of residual monomer to commercially acceptable levels and the elimination of any polymer buildup on process lines—were not resolved at the conclusion of the work. These are problems of formulation and process routine rather than an indication of a basic difficulty in the use of radiation as a catalyst, and, as such, they can be solved within the context of end-product property requirements and in conjunction with development of a specific product.

ECONOMICS

Economics were developed for radiation catalysis in a plant that, in concept, reflects the pilot-plant experience and were compared with those for a plant based on conventional initiation as presently practiced. Plants of four different sizes were evaluated—15, 25, 50, and 100×10^6 lb/year, all on a wet basis. Only a minor fraction of the capital cost is associated with polymerization equipment, and capital costs of the two systems were similar, although the radiation-plant capital costs in the 50 and 100×10^6-lb/year sizes were approximately 5% lower. Estimated operating profit was between 5 and 10% higher for the radiation plant in all cases considered, with the difference in catalyst cost a principal contributing factor.

Using an annual cash flow discount of 10%, plants based on radiation catalysis were written off somewhat earlier than conventional plants. One must recognize, however, that this is a comparison of our best assessment of an undeveloped plant for radiation catalysis with a reasonably reliable estimate of the costs of a conventional plant based on present practices. The differences in process economics must therefore be considered to be within the margin of error in the work performed. Despite this uncertainty, it is significant that even with the costs of shielding and the purchase and replacement of the radioisotope, radiation-catalysis production appears to be at least competitive with conventional latex production.

Little effort was devoted in this program to utilization of the characteristics of radiation-induced emulsion polymerization which are expected to result in superior latex properties. Product properties that are available only through this technique may well provide sufficient incentive for conversion to radiation catalysis, thus making process economics a secondary consideration.

It is estimated that an economic advantage equivalent to approximately 2 cents per wet pound of latex can be achieved by exploiting the superior enamel holdout by both increasing the permissible pigment volume content of the paint and substituting larger quantities of extender for more expensive pigments to achieve a given degree of hiding. If further work confirms these results, this benefit alone provides an overwhelming incentive to produce paint latexes by radiation catalysis in preference to conventional means. Alternatively, there may be a marketing advantage in paints exhibiting superior enamel holdout per se, or superior hiding power.

*Enamel holdout is an index of the practicability of a water-based flat paint to serve as a primer for enamel on unpainted woodwork.

Polymer Grafting to Inorganic Substrates*

By R. A. V. Raff, R. V. Subramanian, D. J. Schecter, and M. F. Adams

(Summarized by R. E. Greene)

Supplementary Keywords: *industry, plastics; industry, stone, clay, and glass; polymerization; grafting; cross-linking; physical property;* ^{60}Co.

Abstract: *In an exploratory study on the effect of gamma radiation on the grafting of polymeric resins to inorganic substrates, four groups of materials were studied—resins with active fillers, glass-fiber-reinforced resins, laminated structures, and ion-exchange resins polymerized in the presence of firebrick. Enhancement of some of the physical properties of the materials was observed. This is a summary of USAEC Report RLO-2098-1.*

Washington State University, under contract to the USAEC Division of Isotopes Development, has investigated the feasibility of gamma irradiation to enhance the useful physical properties of inorganic-filler–polymeric-resin composites by grafting of organic polymers to inorganic substrates. In earlier work[1] on this project, a critical study was made of the literature on polymer grafting onto inorganic materials. This literature study provided ample evidence that unusual properties may be expected in combinations of organic–polymeric and inorganic materials and that high-energy radiation is a suitable source of energy to promote these mixed grafting reactions. The method offers the possibility of varying some physical properties without affecting others. The overall objective was that the results of the work should be of potential interest to industry.

In the most recent work, laboratory studies using radiation were made in four areas—preparation of active fillers for resins, pretreatment of glass fibers used in reinforced resins, preparation of high-temperature-resistant and/or high-strength mixed grafts, and preparation of ion-exchange resins grafted onto porous ceramics.

IRRADIATION OF SPECIMENS

Specimens were irradiated in the ^{60}Co source facility located in the reactor pool at Washington State University. Features of the facility, which is designed for maximum safe storage of 15 thousand Ci of ^{60}Co, are shown in Fig. 1. The geometric relationship of the source to the usable radiation area is shown in Fig. 2.

The specimens were contained in glass or polyethylene vials mounted on a rotating platform of a carrier that was lowered down the lead tube to the radiation area. Uniform irradiation of the specimens was assured since all containers rotated around the central shaft and each container revolved about its own axis.

Gamma-radiation doses received from the ^{60}Co source were read from a plot of the dose vs. month of the year. The plot was constructed from the half-life of ^{60}Co and the initial dose rate determined by the Health Physics Department of Washington State University. Dose rates were approximately 1 Mrad/hr.

EXPERIMENTAL RESULTS

Active Fillers for Resins

Irradiation was used for the preparation of "active" fillers for resins—carbon black for polystyrene and aluminum oxide and carbon black for polyethylene.

With the first two combinations, a master batch technique was used—polymer highly loaded with the filler was molded, irradiated, broken up, and then blended with unirradiated polymer for molding into test specimens with the desired ratio of filler to resin. This technique, in which a highly loaded polymer is irradiated and then diluted with unirradiated polymer, decreases the amount of polymer requiring irradiation and also prepares "active" fillers as commercial products, which, when incorporated in a resin, will lead to superior strength and reinforcement. A 50–50 polystyrene–carbon-black master batch was used for making further blends of 85–15 polystyrene–carbon-black composites for testing. Without irradiation, final strengths were lower for carbon-black-filled samples than for polystyrene alone. Conversely, the modulus of elasticity increased upon the addition of filler. With irradiation at doses in the range 10^6 to 10^7 rads, the tensile and flexural strengths did not change significantly. However, the compressive strength and

*Summary of USAEC Report RLO-2098-1, Washington State University, Pullman, Jan. 31, 1970.

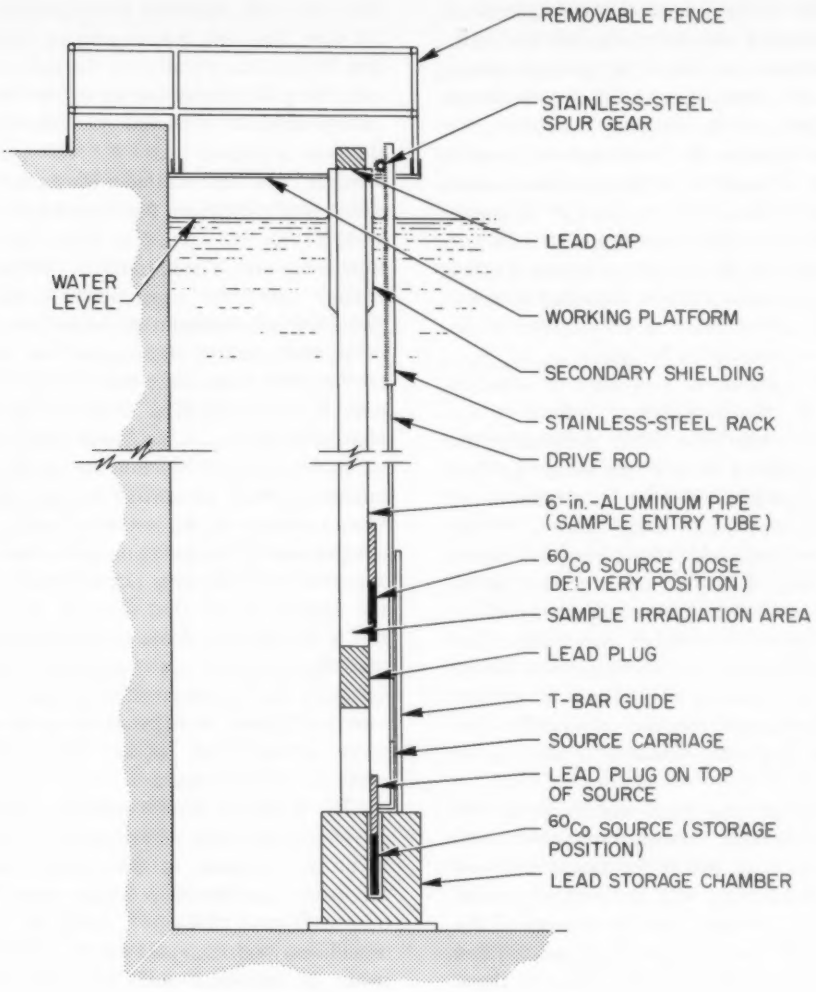

Fig. 1 Cobalt-60 source facility.

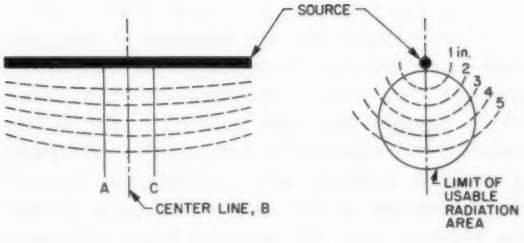

Fig. 2 Geometric relationship of the source to the radiation area: 1, 2, 3, 4, and 5 are isodose curves; A and C define the region in which the isodose curves are essentially straight lines. (Reproduced from C. M. Botchek, C. F. Konzak, and R. N. Nilan, Design of the ^{60}Co Facility at Washington State University, Engineering Paper No. 1064, McDonnell-Douglas Aircraft Corp., Missile and Space Systems Division.)

modulus, and also the tensile modulus, decreased at first and then increased with increasing radiation dose. The flexural modulus, on the other hand, increased somewhat with low doses of radiation but decreased with higher radiation doses. Changes in conductivity followed the same trend as the tensile and compressive moduluses. Over a moderate range, irradiation thus allowed variation in the tensile modulus of the specimens independent of other properties. This behavior might be of interest in the use of carbon-black-filled polystyrene as an adhesive in cable sheathing or in the incorporation of carbon black in polystyrene to increase resistance to degradation by light.

This selective response of properties to radiation was observed in the low-density polyethylene–aluminum oxide system also, thus permitting the preparation of a material with all the advantages but none of the disadvantages caused by the addition of filler. Specifically, specimens made from a 75–25 polyethylene–aluminum oxide blend, prepared from a 20–80 polyethylene–aluminum oxide master batch, showed flexural and compressive strengths as well as modulus values considerably higher than those of the unfilled base polymers but considerably lower tensile strengths. However, when irradiated master batches were used, tensile-strength recovery was nearly complete while other properties remained at their higher values.

In the study of the third combination, the polyethylene–carbon-black system, specimens containing 30% carbon black and 70% polyethylene were prepared and tested directly with and without irradiation treatment. The strengths and moduluses of the filled polymer were higher than those of unfilled polyethylene. Upon irradiation with a dose of about 10^8 rads, further drastic increases in all properties compared with those of unfilled unirradiated polyethylene were observed—from 15 to 85% in the strength values and from 76 to 157% in the modulus values.

GLASS-FIBER-REINFORCED RESINS

Irradiation of glass-fiber-reinforced polyester resin decreased the tensile and flexural strengths and moduluses somewhat but increased the compressive strength and modulus. Treatment of glass fiber with a silane before incorporation into the resin also caused a reduction of all the strengths and moduluses. The mechanical-strength values obtained by reinforcement with glass fiber preirradiated in air did not differ significantly from values obtained when untreated glass fiber was used. Attempts were therefore made to coat the glass fiber with grafted polymer by gamma irradiation before incorporation in the polyester resin. However, no graft polymerization of methyl methacrylate, methyl acrylate, or styrene was initiated by glass fiber that was irradiated (6.3×10^7 rads), cooled in liquid nitrogen, and then treated with monomer in vacuum. These results indicated that free radicals or other active sites, if they are formed at all on the irradiated glass fiber used, viz., Vitro-Strand G, did not survive long, enough under the experimental conditions, even at liquid-nitrogen temperature, to initiate polymerization of styrene, methyl methacrylate, or methyl acrylate. On the other hand, when the fiber had been pretreated with $K_2Cr_2O_7$–H_2SO_4, according to the method of Higashide and Kanazawa,[2] and then irradiated under vacuum, subsequent reaction with methyl methacrylate initiated a small amount of polymer formation (1%). When styrene was used instead of methyl methacrylate, a larger amount of graft polymerization was observed, almost all of it certainly due to acidic sites formed on the surface of the glass fiber by the treatment with $K_2Cr_2O_7$–H_2SO_4. It was concluded from these results that further work can profitably be directed to achieving graft polymerization to glass by irradiating a variety of glasses of different compositions, preferably with simultaneous vapor-phase contact of the monomer with the glass.

The effect of gamma radiation on Vitro-Strand G glass-fiber-reinforced polyethylene of low density was in distinct contrast to that found earlier with the thermoset cross-linked polyester resin. With doses of 6.1×10^7 and 8.4×10^7 rads, all strengths and moduluses were increased up to 54 and 65%, respectively, as compared with those of the unirradiated material. These property values were also greater than those of unfilled, unirradiated polyethylene, whose strengths and moduluses, except the flexural modulus, were decreased by incorporation of filler in polyethylene. The remarkable improvement in properties achieved by irradiation must originate from some or all of the phenomenons discussed—general change due to cross-linking of polyethylene, stronger adhesion due to graft-polymer formation, and reduction in stress and strain concentration in the vicinity of the filler by the formation of a zone of increased density of cross-linking between the resin and filler. The results indicate that development of low-density polyethylene by radiation treatment into a construction material with considerable surface hardness, resistance to abrasion, reduced creep, and increased fatigue endurance should be possible.

HIGH-TEMPERATURE-RESISTANT, HIGH-STRENGTH MIXED GRAFTS

Three different series of experiments were made on the radiation synthesis of high-temperature-resistant and/or high-strength mixed grafts.

In the first experiment, carbon-cloth- and graphite-cloth-reinforced phenolic resin laminates were subjected to 9.3×10^7 and 9.6×10^7 rads of gamma radiation, respectively, after moderate or intense precuring by hot pressing. The strengths of the specimens compared with those of the oven-postcured material showed modest improvement—about 5%. The radiation effect appeared more pronounced on the moderately precured specimens than on the intensely precured specimens and was more apparent when graphite cloth was used. Electrical-resistivity measurements showed no difference between oven-postcured and radiation-postcured specimens. It is possible that much more significant increases in strength might be obtained with higher doses of radiation.

In a second experiment, attempts were made to graft an epoxide resin to metals by gamma radiation for possible improvement of bonding strength. Metal–epoxide castings were irradiated, and the metal–resin joint strength was determined by cleaving with a knife edge. The strength of joints increased many fold with all the metals used—from 160% for copper to 380% for stainless steel. The process has good potentialities for commercial development, especially in encapsulation of stress-sensitive electronic components.

In the third experiment, acrylonitrile was absorbed in porous carbon by vacuum impregnation and polymerized in the pores by gamma irradiation. The specimens were then heated to convert the polyacrylonitrile in the pores to a heat-stable, cyclized, ladder-type polymer. Subsequent tests of density, compressive strength, and chemical resistance showed excellent improvement. Electrical-resistivity values changed little, and no adverse effects were observed when the specimens were used as electrodes and overvoltages were measured. These results argue well for the use of gamma radiation to produce impervious graphite and carbon, which have such important applications in the chemical industry. The low viscosity of acrylonitrile throughout polymerization enables efficient penetration of all pores of the carbon. The excellent heat stability of polyacrylonitrile is an added advantage. The reduction in polymerization efficiency after each impregnation when conventional catalysts are used in this system can thus be obviated by using gamma radiation.

Ion-Exchange Resins

An evaluation was made of the possibility of obtaining ion-exchange materials by using gamma radiation to graft monomers or polymers, capable of ion exchange, to porous ceramics. Sipomer SVS (sodium vinylsulfonate), a strong-acid cation exchanger, and Sipomer Q-1, a strong-base anion exchanger [$CH_2 = C(CH_3)COOCH_2CH(OH)CH_2 \cdot \overset{+}{N}(CH_3)_3Cl^-$], were used as monomers and polymerized in the presence of crushed ceramics and firebrick and a cross-linking monomer, either 1,3-butylene dimethacrylate (BDMA) or N,N′-methylenebisacrylamide (MBA). Near-theoretical ion-exchange capacities were obtained when MBA was used with SVS or Q-1 on 160/200-mesh firebrick polymerized by radiation. Owing to lack of time, radiation polymerization of the ion-exchanging monomers in large porous ceramic structures was not attempted.

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Development of a Radioactive-Pebble-Bed Chemical-Reactor System–Phase III*

By J. Y. Yang, H. T. Cullinan, C. C. Thomas, Jr., and B. F. Ives

(Summarized by Martha Gerrard)

Supplementary Keywords: *synthesis; industry, chemical; energy source, beta;* ^{90}Sr.

Abstract: *The results of tests on a bench-scale chemical reactor containing radioactive microspheres as the energy source to initiate the side-chain chlorination of toluene indicated that such a system is technically feasible. However, the* ^{90}Sr *silicate microspheres used were unsuitable because of a high attrition rate, and no attempt can be made to extrapolate the process to an industrial scale until suitable particles become available.*

The use of radioisotopic energy sources as initiators for chemical reactions of commercial significance is of interest to both the USAEC and the chemical industry. To be commercially attractive, the ionizing-radiation-initiated reaction must be more convenient or more economical than reactions initiated by other means—photolysis, heating, or catalysis. Chlorination of toluene in the side chain, to form benzotrichloride ($C_6H_5CCl_3$), was selected as a process for use in demonstrating the efficiency of a radioisotopic pebble-bed chemical reactor, i.e., a system in which the chemical reactants are intimately mixed with radioactive microspheres, the energy source.

A literature survey[1] indicated that side-chain chlorination of toluene to form benzotrichloride occurs readily at temperatures above 80°C. Since gamma radiation is 8.5 times as efficient in the chlorination of benzene as ultraviolet light (the most efficient energy other than ionizing radiation), an investigation of ionizing radiation for side-chain chlorination of toluene was indicated. However, beta radiation, rather than gamma, was selected as the energy source for the work reported here to minimize the shielding required for the chemical reactor and to enable a larger fraction of energy deposition within the reaction medium in a reactor of reasonable dimensions.

A study[2] of the kinetics of the desired chlorination reaction and the determination of expansion characteristics of a pebble-bed chemical reactor was undertaken by Western New York Nuclear Research Center under contract to the USAEC Division of Isotopes Development. In these preliminary tests, the energy source was 1-MeV electrons from a Van de Graaff accelerator, simulating the beta-emitting radionuclide ^{90}Sr. When the results of the tests indicated that reaction efficiencies might be sufficient for industrial economic use, a bench-scale pebble-bed chemical reactor using actual radioactive microspheres was designed and constructed for the side-chain chlorination of toluene. The construction and preliminary testing of this chemical system are described here.

CHEMICAL-REACTOR-SYSTEM DESIGN

In the pebble-bed toluene-chlorination reactor, a mixture of liquid toluene and gaseous chlorine is dispersed on radioactive microspheres ("pebbles"), where the radiation energy causes the chlorine to substitute for the hydrogen in the methyl side group of the toluene. The microsphere bed is fluidized and expanded as the reacting mixture is pumped upward in the reaction chamber.

The bench-scale system was designed to permit operation under a range of conditions—varying reactor height, column diameter, reactant flow rate, and source strength. Production rates were not specified for this preliminary model.

The fission product ^{90}Sr–^{90}Y was selected as the beta-radiation source because its half-life is conveniently long—28.8 years—and it is available as strontium silicate microspheres.

Chemical Reactor

The bench-scale chemical reactor was a 1-liter Pyrex-glass column (Fig. 1). The temperature was controlled by ethylene glycol–glycerol from a thermostatted bath, which circulated in a cooling jacket. The microspheres were in the main portion of the column, which contained a removable insert with a fritted-glass bottom.

*Summary of USAEC Report NYO-3864-2, Sept. 15, 1970, Western New York Nuclear Research Center, Inc., Power Drive, Buffalo, N. Y. 14210.

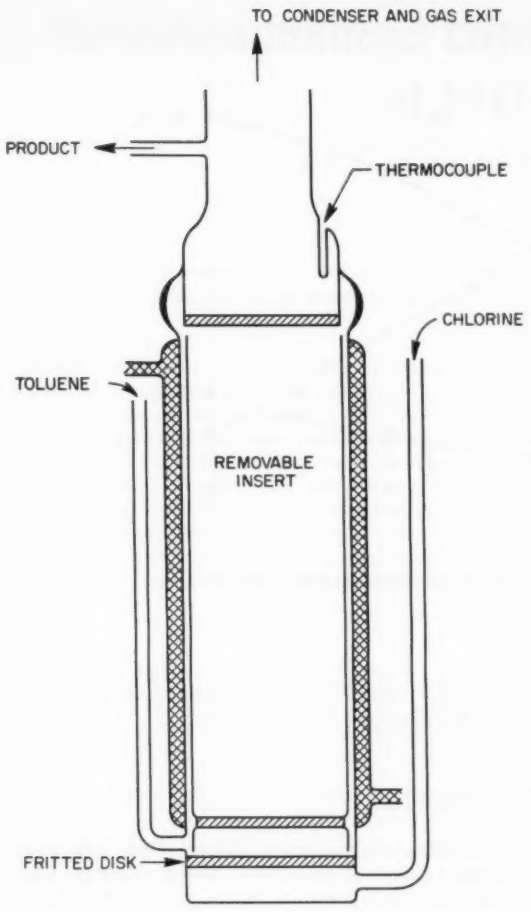

Fig. 1 Bench-scale pebble-bed chemical reactor, 2 in. in diameter by 20 in. high, used in studying beta-radiation-initiated chlorination of toluene.

The lower part of the column was separated from the main portion by another fritted-glass disk. This formed a chamber where the organic liquid mixed with the chlorine gas. Chlorine was fed into this mixing chamber through a Drierite column, and the toluene through a preheater (80°C) and a rotameter. The toluene flow rate was sufficient to fluidize and expand the bed of microspheres. The product benzotrichloride went out the top of the reaction chamber and was collected. The off-gas, containing unreacted chlorine and hydrogen chloride produced in the substitution reaction, went through a condenser at 0°C and then through a chain of scrubbers before being released to the air.

Radiation Source

Kinetic studies had indicated that a G* value of 10^5 for benzochloride production could be achieved with a radiation intensity of 10^{18} eV/(mole)(min), which would require 10 Ci of ^{90}Sr–^{90}Y uniformly distributed throughout the substrate, toluene. A source particle specific activity of 0.5 Ci/g was selected so that a range of radiation intensity could be achieved without significantly varying the bed height. The initial 5-Ci loading was obtained by using 90 g of inactive and 10 g of active strontium silicate. Subsequently, inactive beads may be added to decrease the average specific activity and the dose intensity per unit volume. With strontium microspheres of 2.0 g/cm^3 bulk density, 100 g of beads would give a settled bed height of 1 in. in the 2-in.-diameter reactor. The beads tested had an average particle density of 2.90 g/cm^3, giving a bulk density of 2.0 g/cm^3 in accordance with cubic close packing of spherical particles. For high utilization efficiency of the beta radiation, the linear bed expansion should be at least 10. A toluene flow rate of 2 gal/min would give a linear bed expansion of 8.

SYSTEM TESTS

All chlorination experiments were made with unclassified microspheres, as received. A majority of these experiments were carried out with 150 g (5 Ci) of ^{90}Sr–^{90}Y particles being fluidized with 2.5 liters of toluene. The chlorine flow rate was 2 liters/min, the highest rate that could be maintained in our reaction system. The ^{90}Sr silicate microspheres used were not homogeneous in size, and attrition was severe under the conditions used. Nevertheless, the feasibility of the concept of a radioactive-pebble-bed chemical reactor for chlorinating toluene was demonstrated.

In a typical 8-hr run, 80% of the toluene was converted to the monochloro derivative, 15% to the dichloro derivative, and 5% remained unreacted (Fig. 2). No benzotrichloride was obtained. An 8-hr reaction with a 5-Ci source corresponds to a release of 1×10^{21} eV of energy (5×10^{20} eV/hr). In the 8-hr run, 27 moles of chlorine was consumed, only 75% of that put into the system. Chlorine could be introduced at a faster rate with a more efficient gas-mixing system.

The potential usefulness of a radioactive-pebble-bed chemical-reactor system cannot be assessed until

*The G value is the number of chlorine atoms substituted into the toluene side chain for each 100 eV of energy deposited in the reaction system.

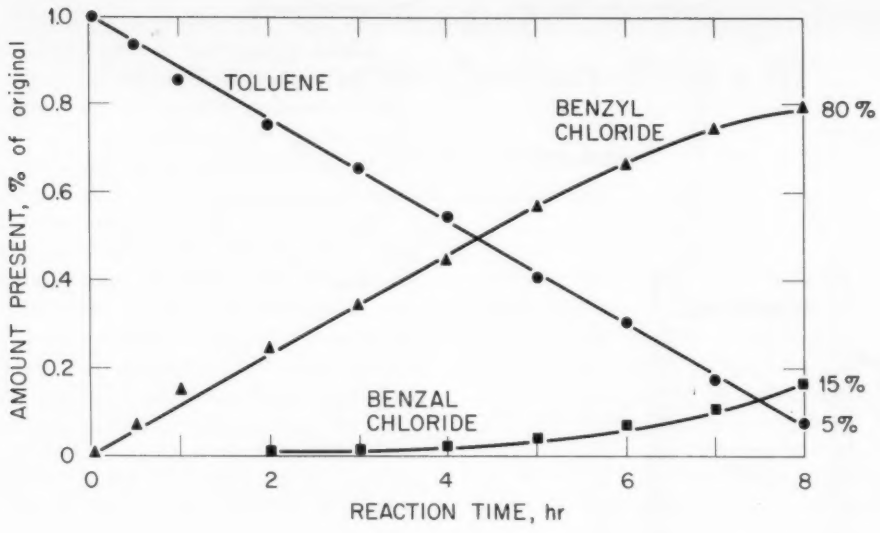

Fig. 2 Chlorination of toluene to benzyl chloride ($C_6H_5CH_2Cl$) and benzal chloride ($C_6H_5CHCl_2$) as a function of time.

satisfactory immersible radioactive sources are available. Those used here were unsatisfactory because of the wide density and size variations in the particles; the presence in almost all particles of voids and other structural defects, which caused severe bead attrition during fluidization; and particle degradation on prolonged exposure to acids and possibly other chemicals. Carefully classified strontium silicate microspheres could be used as the radiation source, but the added costs for classification would increase the process costs. Borosilicate and silica glasses labeled with ^{90}Sr–^{90}Y, which are chemically inert under most conditions, might be suitable. If satisfactory immersible sources should become available, only a limited effort would be needed to develop radioactive-pebble-bed chemical-reactor systems.

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Radiation-Induced Oxidation of Process Effluents at High Pressure*

By F. N. Case,† D. L. Kau,† D. E. Smiley,† and A. W. Garrison‡

Supplementary Keywords: *industry; industry, textile; industry, paper; industry, utility; pollution; water and waste treatment; ^{60}Co.*

Abstract: *High-pressure radiation-induced oxidation has been shown to decrease the pH, biological oxygen demand, and chemical oxygen demand in textile-mill, paper-mill, and municipal sewage-plant effluents more than a similar irradiation at atmospheric pressure. Sedimentation rates of solids in effluents from cotton-textile-finishing mills were greater at high pressure than at atmospheric, and color due to residual dye compounds was better removed from textile effluents. Color and odor were also removed from paper-mill waste and municipal sewage to a much greater extent at high pressure than at atmospheric pressure.*

Most of the gamma-irradiation experiments using ^{60}Co or ^{137}Cs to sterilize sewage and to aid in dewatering sludge and altering detergents have been carried out at atmospheric pressure.[1-4] The work at Oak Ridge National Laboratory, in cooperation with the U. S. Department of the Interior, Southeast Water Laboratory, and under the sponsorship of the Division of Isotopes Development, has been to study the oxidation of process effluents under the influence of gamma radiation at high oxygen and air pressures. The results of tests on color removal and decrease in biological oxygen demand (BOD) and chemical oxygen demand (COD) and on color removal in kraft-paper-mill effluent, municipal sewage-plant effluent containing sulfite-paper-mill waste, and textile-mill effluents are reported here.

SAMPLE-IRRADIATION PROCEDURES

For irradiating samples under pressure and mechanically static conditions, a Parr pressure vessel containing a 500-ml glass liner was used. (A flow-through high-pressure irradiator is being used in current studies.) In the Parr vessel, oxygen or air at pressures up to 2000 psi can be mixed with effluent samples and delivered to a pressure vessel placed in a water-shielded ^{60}Co irradiator loaded with approximately 120 thousand Ci of ^{60}Co. The radiation dose inside the pressure vessel was 6.8×10^6 to 8×10^6 R/hr. Temperature was controlled at 30 to 36°C by the temperature of the water that shielded the irradiator.

Irradiations at atmospheric pressure were made in a glass vessel placed in the ^{60}Co irradiator. In the absence of the thick-walled pressure vessel, the dose rate was approximately 1×10^7 R/hr inside the glass vessel.

Irradiated samples were evaluated for 5-day BOD and for COD by standard methods.[5] The percentage of light transmitted was measured on a spectrophotometer or calculated from absorption curves. Dieldrin concentration in aqueous samples and textile-mill effluents was measured by extracting the Dieldrin into hexane and drying with sodium sulfate for injection into gas-chromatograph equipment having an electron-capture detector.

Municipal Sewage-Plant Effluents

Since the use of radiation processing methods to treat the very large volumes involved in municipal sewage-treatment plants does not appear to be economically favorable[6] at this time, emphasis was placed on the high-pressure oxidation of specific industrial effluent streams that are difficult to process by conventional methods and where volume can be controlled by isolation of these streams. The material for irradiation was highly colored effluent from a Knoxville, Tenn., municipal sewage-treatment plant. The principal color-producing components were from a sulfite paper mill that discharged waste effluent directly into the sewer system feeding the treatment plant. Minor color pollutants were from chicken-processing industries. The results of irradiation at 36°C in air at atmospheric pressure and at 2000 psi showed a definite improvement in *p*H, a decrease in BOD and COD, and better color removal at the high pressure than at atmospheric pressure (Table 1).

*Summary of paper presented at IAEA Symposium on the Use of Nuclear Techniques in the Measurement and Control of Environmental Pollution, Salzburg, Austria, October 1970.

†Oak Ridge National Laboratory, Oak Ridge, Tenn.

‡U. S. Department of Interior, Southeast Water Laboratory, Athens, Ga.

Table 1 Effect of Pressure During Gamma (^{60}Co) Irradiation of Sewage-Plant Effluent Containing Sulfite-Paper-Mill Waste

Gamma dose, rads	Conditions	BOD, ppM	COD, ppM	*p*H	Light transmission, % 280 mμ	400 mμ	500 mμ	625 mμ
	Control	202	720	7.1	0	22	48	58
2×10^6	1 atm air	128	*	7.1	0	15	43	52
4×10^6	1 atm air	101	*	6.8	0	12	41	51
6×10^6	1 atm air	85	*	6.7	0	5	26	41
1.2×10^7	1 atm air	76	*	6.4	0	8	36	48
2.4×10^7	1 atm air	53	590	6.1	0	5	26	37
1.4×10^6	2000 psi air	166	*	6.6	0	26	50	54
2.8×10^6	2000 psi air	140	*	6.1	<1	38	62	62
4.2×10^6	2000 psi air	122	*	6.0	8	54	68	65
8.3×10^6	2000 psi air	100	*	4.3	25	65	74	71
1.66×10^7	2000 psi air	28	265	3.4	58	83	88	87

*Not measured.

Kraft-Paper-Mill Effluent

Kraft-paper-mill effluents were irradiated in the presence of oxygen, air, and chlorine and evaluated for color removal, solids content, and COD decrease.

Irradiation alone produced only slight decolorization of strongly colored effluents. Color removal was greatest when samples were treated with a combination of oxygen (air or pure oxygen) and gamma radiation, which decolorized even dark-brown opaque kraft effluents to a clear liquid with a very low color value. Irradiation in air under pressure was less effective in removing color than was irradiation in pure oxygen (Table 2). This effect is related to the oxygen available for reaction with the highly colored lignin, as shown in an experiment in which air was bubbled through kraft effluent during irradiation and the sample was decolorized with a radiation dose of approximately half that necessary for decolorization in a mechanically static system.

Oxidation of kraft effluent by saturating the effluent with oxygen without irradiation caused solids to precipitate,[6] but irradiation decreased the solids precipitation (Table 3).

Several experiments were conducted in chlorine and air with irradiation to observe the effects on *p*H, suspended solids, and COD of kraft effluent (Table 4). The principal effect of chlorine either with or without radiation was to lower the *p*H, which caused precipitation of lignin. There appears to be no advantage in the use of chlorine over air or oxygen for decreasing the COD.

Textile-Mill Effluents

Textile-mill effluents consisting of cotton-finishing-plant waste and wool-mill waste were studied. These effluents are usually highly colored owing to the residual dye content and have a high BOD, COD, and *p*H. Because textile dyes are compounded to be chemically stable to the usual conditions of light and oxidation and to reactions with water as well as to biological activity, the destruction of color in textile effluents is difficult. While the BOD and COD for most dyes are low (a 1-lb mixture of 18 different dyes yields[8] a 0.07-lb BOD), the pollution potential from color is severe.[9] Irradiation alone produced some color change in the effluents and a decrease in BOD; however, the effect was much greater when the same amount of radiation was applied to the effluent under 1500 psi O_2 (Table 5). Doubling the radiation dose to the effluent under 1500 psi O_2 provided a further color reduction, but only a slight change in BOD. There was a further decrease in *p*H, which indicates that organic acids were produced as a result of the oxidation process.

Examination of samples under the microscope showed larger and more numerous solid particles in the irradiated samples than in the controls. The volume of solids and the rate at which they settled from irradiated samples were significantly greater than in the control samples.

Wool-mill effluents are generally difficult to process by conventional waste-treatment methods. Wool-scouring wastes have high solids and grease content and

high BOD and are often combined with total wool-mill waste to yield highly colored effluents. Gamma irradiation in the presence of air or oxygen removed color from aqueous solutions of pure dyes and from wool-dye-waste samples (Table 6). The red dye was decolorized in 1 min by a combination of radiation and oxygen pressure. Radiation alone decolorized the bright-orange–dye vat waste. The yellow-gold–dye vat waste was decolorized in 15 min with a radiation dose of 8×10^6 R/hr, but an 18-hr exposure of the sample to pure oxygen at 2100 psi without irradiation produced no color change. In a mechanically static system, a 2.5-ml sample was decolorized by 25% of the dose required for a 5-ml sample, although the areas of

Table 2 Decoloration of Kraft-Paper-Mill Effluent by Gamma (^{60}Co) Irradiation in Oxygen or Air

Gamma dose, rads	Conditions	Light transmission, %				
		320 mμ	415 mμ	510 mμ	605 mμ	700 mμ
	Control	0	0	6	10	26
4×10^6	2000 psi air	0	0	8	38	63
16×16^6	2000 psi air	0	8	46	68	80
16×16^6	500 psi O_2	18	58	74	80	83
16×10^6	2000 psi O_2	42	82	88	94	96

Table 3 Effect of Pressure During Gamma (^{60}Co) Irradiation on Solids Precipitation from Kraft-Paper-Mill Effluent

Gamma dose, rads	Conditions	*p*H	Solids precipitated, mg/ml	COD, mg/liter
	Control	9.08	48	3218
0	1900 psi 0_2	8.19	264	2846
4×10^6	2000 psi O_2	7.52	34	2461
8×10^6	2000 psi O_2	7.30	60	1920
1.3×10^7	2000 psi O_2	7.33	74	1379
1.6×10^7	500 psi O_2	7.05	104	1092
1.6×10^7	2000 psi O_2	7.30	59	1152

Table 4 Effect of Chlorine on COD Decrease by Gamma (^{60}Co) Irradiation of Kraft-Paper-Mill Effluent

Gamma dose, rads	Conditions	*p*H	Solids precipitated, mg/ml	COD, mg/liter
	Control	9.08	48	3218
0	Bubbling Cl_2	3.73	680	2875
4×10^6	2000 psi Cl_2	2.98	642	2442
4×10^6	2000 psi air	7.58	140	2410
8×10^6	Bubbling air	8.64	152	1260
1.6×10^7	2000 psi air	6.06	78	1841

Table 5 Effect of Pressure on Gamma (^{60}Co) Irradiation of Cotton-Mill Effluents in Air or Oxygen

Gamma dose, rads	Condition	Irradiation time, hr	*p*H	COD ppM	BOD ppM	Light transmission, %					
						700 mμ	580 mμ	480 mμ	440 mμ	380 mμ	320 mμ
	Control	–	11.5	1570	1400	49	39	28	21	10	0
0	2000 psi O_2		*	*	1000	*	*	*	*	*	*
8×10^6	Atmospheric, air	3	11.3	1570	180	53	44	33	27	15	2
8×10^6	1500 psi O_2	1	7.4	960	39	60	52	42	32	30	19
1.6×10^7	1500 psi O_2	2	6.7	1130	65	65	57	48	44	38	27

*Not measured.

Table 6 Effect of Pressure on Decoloration by Gamma (^{60}Co) Irradiation of Dyes

Sample	Gamma dose, rads	Condition	Color change: Visual, Original	Color change: Visual, Final	Color change: Light transmission, % 410 mμ	Color change: Light transmission, % 412 mμ
Disperse violet	1.2×10^5		Violet	Colorless	–	–
Acid red (water-soluble azo, 4 mg/ml)	8×10^6		Opaque red	Pale amber		
Red dye, vat waste	1.2×10^5	2000 psi O_2	Bright red	Colorless		
	1.2×10^6	Bubbling air	Bright red	Colorless		
Yellow-gold dye, vat waste	0	1 atm air				8
	0	1600 psi O_2				9
	1.2×10^6	1 atm air				63
	6×10^5	1600 psi O_2				98
Bright-orange dye, vat waste	0	1 atm air			5	
	0	1600 psi O_2			5	
	1.2×10^6	1 atm air			98	
	1×10^6	1600 psi O_2			98	

Table 7 Effect of Gamma (^{60}Co) Radiation Dose and Pressure on Color Removal from Dye Waste Effluent

Gamma dose, rads	Conditions	Sample vol., ml	Light transmission, % 450 mμ	Light transmission, % 380 mμ
	Control		0	0
4×10^5	200 psi O_2	5	23	0
4×10^5	800 psi O_2	5	50	14
4×10^5	1600 psi O_2	5	73	50
8×10^5	1600 psi O_2	5	85	71
1.6×10^6	1600 psi O_2	5	81	74
4×10^5	1600 psi O_2	2.5	81	79

Table 8 Destruction of Dieldrin in Aqueous Medium by Gamma Radiation in a High-Pressure Oxygen Atmosphere

Dieldrin concentration,* ppM	Gamma dose, rads	Conditions	Dieldrin removed, %
20	0	1800 psi O_2 (4 hr)	32.5
20	0	1800 psi air (4 hr)	30.0
20	8×10^6	1 atm air	64.5
20	8×10^6	1800 psi O_2	99.0
20	8×10^6	1800 psi air	98.5
5	2×10^6	2000 psi O_2	97.8
5	4×10^6	2000 psi O_2	98.6

*Samples prepared by dispersing 20% Dieldrin–73% petroleum–7% emulsifiers and stabilizers in water.

the gas–liquid interfaces were identical in the two samples (Table 7). Increasing the pressure increased the decoloration for the same dose.

Because Dieldrin is often used in the treatment of wool to impart mothproof qualities to wool fabric, this pesticide may be found in wool-mill effluents. Destruction of this material by gamma radiation in an air atmosphere was considerably greater at 1800 psi than at atmospheric pressure for the same radiation dose (Table 8). (MG)

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Section

V

Isotopes and Radiation Technology

Source Development

Isotopic Neutron Sources from the Los Alamos Meson Physics Facility (LAMPF)

By H. A. O'Brien, Jr.,* and M. E. Schillaci*

Abstract: *The main beam of the LAMPF accelerator—with approximately 0.5 mA of 700-MeV protons at the main beam stop—will be used for producing radionuclides, primarily by spallation. The principal features of the LAMPF accelerator, the conceptual design of the Isotope Production Facility, and the systematics used to estimate the spallation reaction cross sections are discussed, together with thick-target considerations. The LAMPF machine will make available, in commercially useful quantities, several radionuclides for making photoneutron sources with a variety of neutron energies, one of the more promising being 107-day ^{88}Y. Approximately 75 Ci of ^{88}Y per month can be produced with exceptionally high specific activity from a 1-in.-thick zirconium target. An ^{88}Y–Be source will emit 150-keV neutrons with an intensity of about 3×10^6 n/(sec)(Ci) and apparently can compete favorably with ^{124}Sb–Be.*

The Los Alamos Meson Physics Facility (LAMPF) is a linear accelerator that will accelerate protons to an energy of 800 MeV and have an average beam current of 1 mA. Developed over the past 5 years, the full-energy beam is expected in July 1972, and actual operation is expected to start about January 1973. At the peak usage of this machine, it is anticipated that the residual beam reaching the main beam stop will have approximately 0.5 mA of 700-MeV protons, which can be used for producing radionuclides. Since the cost of prime beam time normally associated with accelerator-produced isotopes is not present here, a substantial economy can be realized. The combination of high energy and high intensity of the LAMPF beam will allow production, in large quantities, of many radionuclides not now available.

The largest proton linear accelerator now in existence with a comparable current has an energy of only 68 MeV. The only accelerators that approach the LAMPF in operating characteristics are the machines being built in Zürich and in Vancouver (TRIUMF) and the soon-to-be-completed modified synchrocyclotron of Columbia University. However, these projects are designed for peak energies several hundred MeV lower than that of the LAMPF, and the external beam intensities are a factor of 10 less for the Zürich accelerator and TRIUMF and a factor of 30 less for the Columbia machine.

The utility of the LAMPF for producing selected radionuclides that can be used as the active components in low-energy (<1 MeV) photoneutron sources is pointed out here. Many such sources have been described in the literature.[1] However, because the radionuclides used cannot be economically produced with sufficiently high activities or because they have very short half-lives, almost none are commercially useful. One source that is readily produced in reactors at relatively little cost, that has a half-life of 60 days, and that has proved useful in several applications is ^{124}Sb–Be. We present here a list of several gamma emitters with at least several-day half-lives, which can perhaps be economically produced with sufficient activity to provide additional useful isotopic neutron sources with a variety of neutron energies.

*Los Alamos Scientific Laboratory, Los Alamos, N. Mex. 87544. This work (Report LA-DC-11982) was reported at the American Nuclear Society's National Topical Meeting on Neutron Sources and Applications, Augusta, Ga., Apr. 19–21, 1971, and published in the proceedings.

DESCRIPTION OF LAMPF

The LAMPF accelerator (Fig. 1) is approximately 0.5 mile in length and is composed of three separate accelerators, each optimized for a particular energy range. First is a conventional Cockcroft–Walton injector, by means of which protons will be accelerated to 0.75 MeV. These protons will be injected into a modified "Alvarez" structure—named after its inventor, Professor Luis Alvarez of Berkeley—which will accelerate the protons to 100 MeV. From here the beam will go to a wave-guide section, a side-coupled cavity system developed at Los Alamos and characterized by good stability and high efficiency for transforming the 800-MHz r-f power into beam power. Plans call for the first beam in July 1972.

The main purpose of the facility is to provide sufficient intensities of nucleons, pions, muons, and neutrinos to make possible their use as probes to explore the structure of the atomic nucleus and the forces by which this structure is governed. Consequently, several experimental areas are planned (Fig. 2), each requiring particular beam energies and intensities. A complex system of bending magnets and quadrupole lenses will transport the proton beam to the various experimental locations, and several innovations will allow portions of the 500-μsec beam to be deflected to experimental areas requiring only a small amount of beam.

Along the main high-intensity proton-beam path, at least six experiments will use the same beam. After each target, the beam will be refocused and transported to the next target. Even so, a major portion of the proton beam will remain and must be disposed of. Therefore it is proposed to locate an Isotope Production Facility (Fig. 3) at the end of the main proton channel, which will use the excess protons to prepare a wide variety of both neutron-deficient and neutron-excess radionuclides. Recent estimates indicate that, when all the target stations upstream of this facility are occupied, the beam reaching this facility will contain protons of 700 ± 20 MeV at a current of 400 ± 100 μA.

The target assembly of the Isotope Production Facility will provide for six target stations, each independently operated. This independent operation will permit choosing the optimum irradiation time for each target–product combination, as well as for insertion and removal of targets from the beam without interrupting the irradiations in the other stations. Each

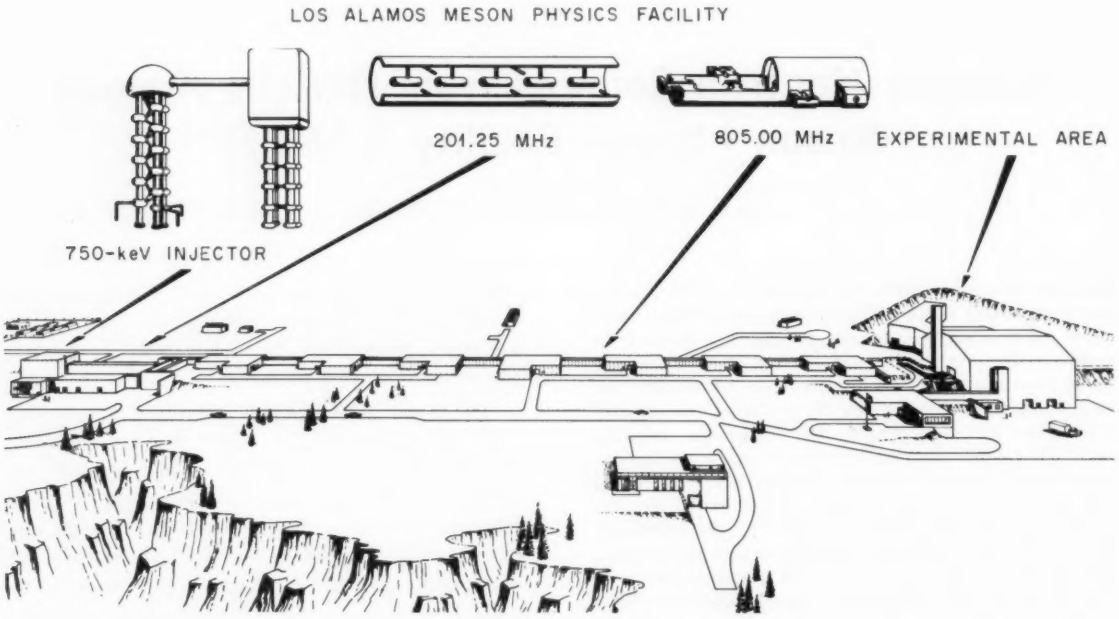

Fig. 1 Schematic representation of the three major components of the LAMPF accelerator.

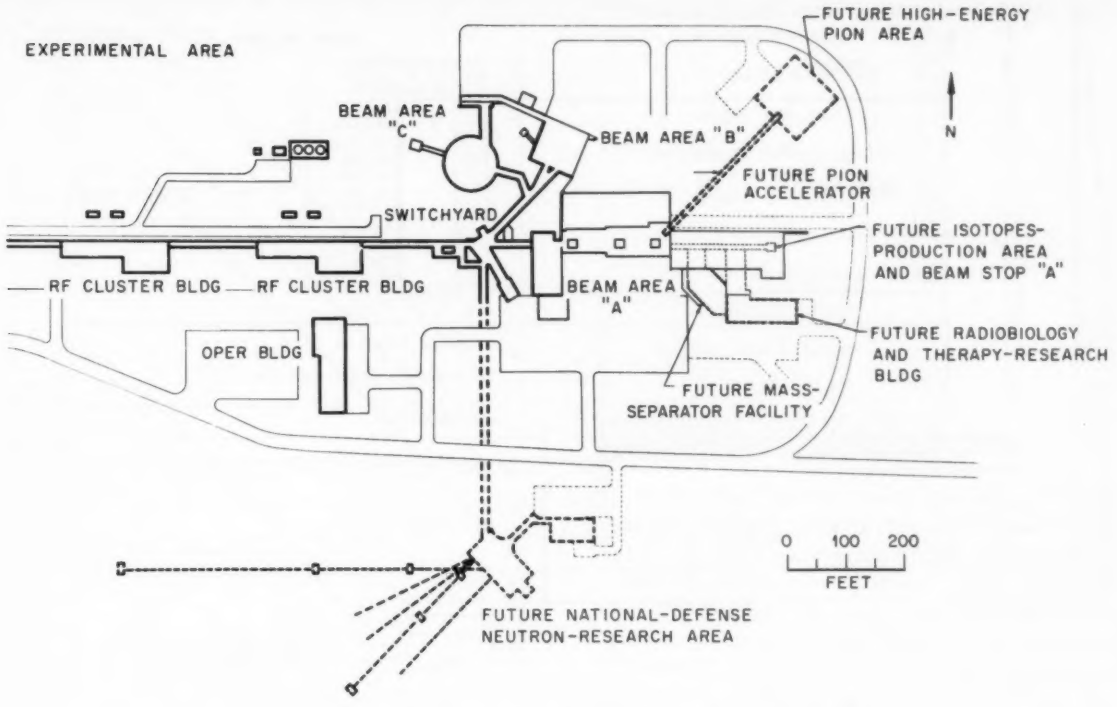

Fig. 2 LAMPF Experimental Area showing the location of the Isotope Production Facility.

target station will accommodate a target or combination of targets up to about 1 in. thickness and will contain provisions for target cooling, instrumentation, and a mechanism to remove the target station from the proton beam when not in use. One or more of the target stations will probably be equipped for continuous removal of gaseous products during bombardment.

Taking into account both beam attenuation and scattering, calculations indicate that if 700-MeV protons enter the first target station, approximately 500-MeV protons will exit from the sixth target. Also, the sixth target will see about 20% of the beam that impinges on the first station.

Yield Predictions

The principal reaction in the production of radionuclides at LAMPF is high-energy proton-induced spallation. In this reaction, many nucleons are knocked out of the nucleus, both singly and in clusters, resulting in a variety of possible nuclei. The mass-yield curves from a bismuth target at several energies, as shown in Fig. 4, are examples. Here the 800-MeV curve has been sketched in to provide a qualitative comparison with the curves representing data. The general features to be noted are (1) a peak corresponding to spallation products near the target mass; (2) another peak (for higher mass targets) corresponding to fission products at intermediate masses; and (3) a rise at the low-mass end corresponding to fragmentation products. It is the region of the first peak—spallation products—that is of interest here.

Since available cross-section data at or near 700 MeV are insufficient for most of the target–product combinations of interest, we have used the empirical systematics developed by Rudstam[3] to calculate, rapidly, the approximate yield predictions. Rudstam's empirical formula, which was meant to be used only for products that are 3 or more mass units removed from the target, represents approximately 1200 data points available at the time and was shown to be accurate to within a factor of 2 or 3 for almost all the data. The accuracy tends to degenerate for low-mass targets because of the contribution of secondary particles and for high-mass targets because of the importance of fission. Within these restrictions, it is

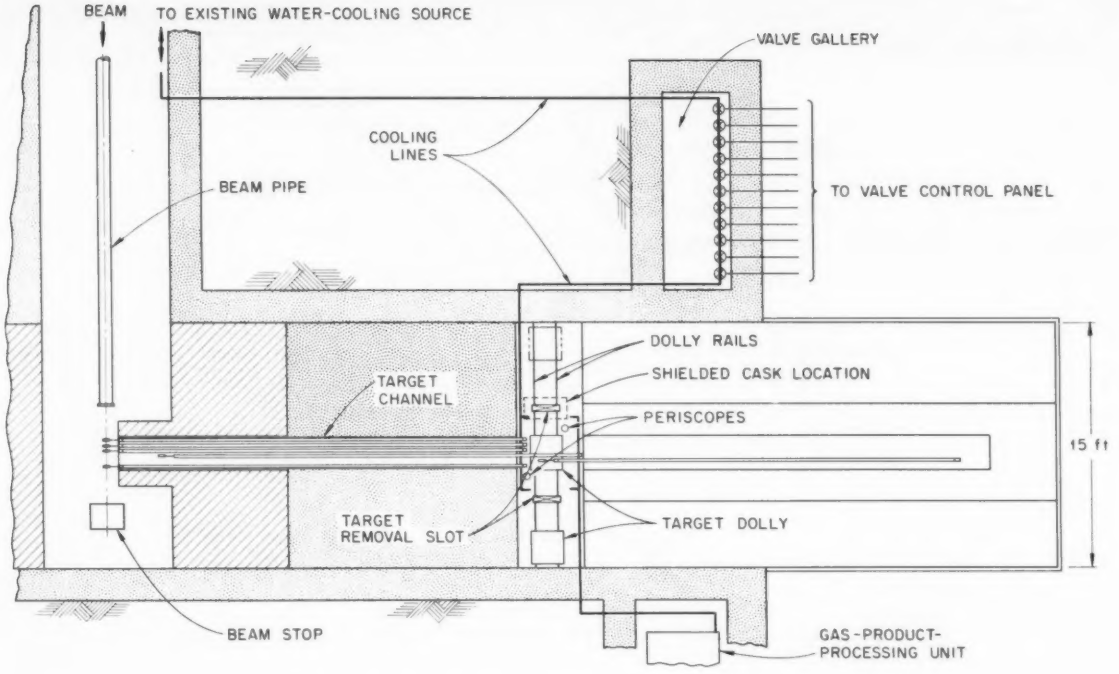

Fig. 3 Proposed target assembly for the Isotope Production Facility.

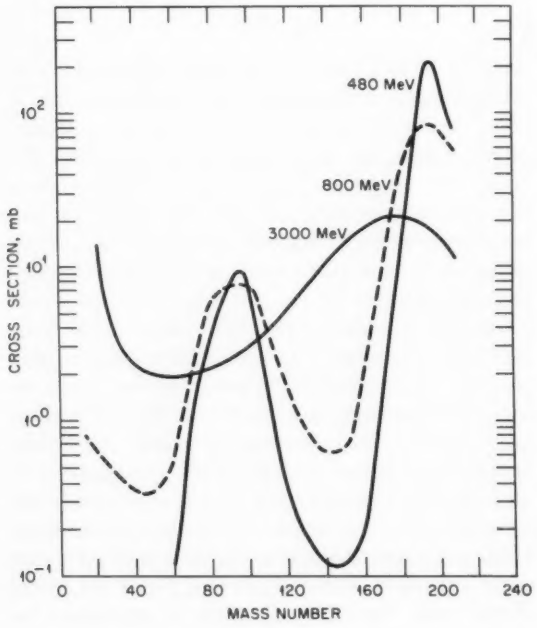

Fig. 4 Mass-yield curves for the proton bombardment of bismuth.[2]

felt that Rudstam's systematics are useful for estimating spallation cross sections for most target–product combinations. The formula was programmed so that the cross section could be calculated from incident energy, target mass, and product mass and charge. A refinement to Rudstam's formula made by Chackett and Chackett,[4] which takes into account the charge of the target, was also included in our program. This program has been used to calculate the cross sections of products lying within 40 mass units of each of about three dozen targets.

The calculations described above refer to thin-target cross sections. Since the production targets to be used at LAMPF will be relatively thick (~1 in.), some account must be taken of the effective cross section as a function of depth. Some thick-target data, taken by Shedlovsky and Rayudu,[5] are shown in Fig. 5, which indicates the effective cross section for producing various nuclides from a thick iron target with incident protons of 1 GeV energy. The solid curves represent an attempt to fit the data with an empirical formula.[6] An important feature is that, for products with relatively small ΔA ($\equiv A_{\text{target}} - A_{\text{product}}$), there is a buildup in the effective cross section, peaking at about 60 g/cm^2 for the 1-GeV case. This effect is even more

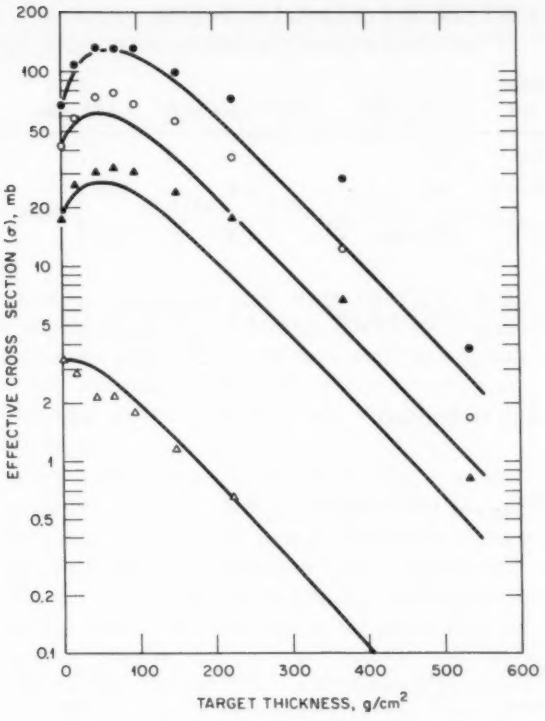

Fig. 5 Thick-target yields in iron at 1 GeV. ●, ^{54}Mn; ▲, ^{52}Mn; ○, ^{51}Cr; △, ^{32}P; ——, empirical formula.

pronounced at higher energies[5] and is believed to be caused by secondary particles producing such nuclides in addition to the primary protons. Since almost all products of interest for us will have a relatively small ΔA, an obviously conservative way of handling the thick-target problem is to assume a constant cross section as a function of depth. In addition, let us assume that this constant is given by the thin-target cross section calculated from the Rudstam systematics—also a conservative estimate since the secondary particles produced in a thick target surely contribute something to the effective cross section. Thus, the most naive approximation for our thick-target cross sections is clearly justified.

The activity produced (Ci) of a specific nuclide is given by

$$Y = \frac{1}{c}\left(\frac{N}{A_T}\rho_T x\right) I(\sigma_0 \cdot 10^{-27}) \times [1 - \exp(-0.693\, t_i/\tau_{1/2})] \quad (1)$$

where $c = 3.7 \times 10^{10}$ and converts disintegrations per second to curies

N = Avogadro's number

A_T = target mass number

ρ_T = target density (g/cm^3)

x = target thickness (cm)

I = beam intensity (protons/sec)

σ_0 = thin-target cross section (mb)

t_i = irradiation time

$\tau_{1/2}$ = product half-life

PHOTONEUTRON SOURCES OF INTEREST FOR LAMPF

In selecting a list of suitable gamma emitters, two criterions are used: (1) a half-life of at least a few days and (2) a gamma energy greater than the threshold for neutron production in ^{9}Be—viz., $E_\gamma > 1.666$ MeV (Ref. 1). Another commonly used material is D_2O; however, since the binding energy of the deuteron is 2.226 MeV, considerably more energetic photons are required to produce neutrons. A list fulfilling these criterions, culled from a standard table of isotopes,[7] is presented in Table 1. The cross sections and yields given in Table 1 are based on the assumptions of a 700-MeV, 0.5-mA proton beam, a 1-in.-thick target, and an irradiation time equal to the product half-life. This choice of irradiation time simplifies the presentation of the results and gives a yield that is half the saturation yield.

It should be noted that the cross sections used for the production of ^{205}Bi and ^{206}Bi from a lead target are surely too high. This is to be expected since the Rudstam formula tends to overestimate the cross section when ΔA is less than 3. In addition, no account is taken of the increased importance of fission for heavier targets, resulting in decreased spallation cross sections. In fact, the results of an intranuclear cascade calculation[8] indicate that the cross sections in question are approximately an order of magnitude lower than indicated by the Rudstam systematics. Nevertheless, we shall use the yields as stated in Table 1, but with a note of caution in the case of bismuth.

The material most commonly used for the production of neutrons by the emitted gamma rays is beryllium. Let us assume, for the purpose of calculation, a simplified model of the photoneutron source in which the radioactive component is enclosed in a spherical volume of beryllium of thickness x. Then the

Table 1 Gamma Emitters of Interest for LAMPF (700 MeV, 0.5 mA; 1-in. Targets)

Product	Half-life, days	Target	σ_0 mb	Gamma energy MeV	Gamma energy %	Yield, Ci*	E_n, keV	10^{-6} n/(sec)(Ci)	10^{-6} n/sec
^{88}Y	107	Zr	45	1.836	99.5	210	151	2.9	610
^{206}Bi	6.24	Pb	77†	1.720	36	450†‡	48	1.8	810† } 1000§
^{205}Bi	15.3	Pb	37†	1.766 1.864 1.906	27 6 2	130†	89 (peak)	1.5	190† }
^{56}Co	77.3	Cu	8.8	1.76 2.02 2.60 3.26	15 11 17 13	79	185,514(D_2O)	1.2	91
^{124}I	4.2	La	32	1.69 2.09 2.26	14 2 1.5	92	21 (peak)	0.73	68
^{156}Eu	15.2	Tb	39	2.187 2.181 2.098 2.026 1.966 1.937 1.877	3.5 2.2 3.9 4.9 4.0 3.1 1.6	130	(7) 188 to 463	0.38	50
^{156}Tb	5.4	Ho	100	1.85	3	340	164	0.080	28
^{119m}Te	4.7	Sb	100	2.09	4	360¶	377	0.053	19¶
^{48}V	16	Cr	32	2.24	3	290	511	0.040	12
^{106m}Ag	8.3	Sb	17	1.83	3	60¶	146	0.087	5¶
^{124}Sb**	60						24	2.8	

*Irradiation time (t_i) = half-life ($T_{1/2}$).
†These figures are probably too high by about an order of magnitude.
‡t_i = 15.3 days.
§These figures are probably too high by about an order of magnitude.
¶These yields should be multiplied by the fraction of the excited state produced relative to the ground state.
**Included for comparison.

intensity of the source per unit activity of the radioactive component [n/(sec)(Ci)] is given by

$$n = cf\left(\frac{N}{A_T}\rho_T x\right)(\sigma \cdot 10^{-27}) \qquad (2)$$

where σ is the (γ,n) reaction cross section at the particular energy of the gamma ray (mb), and f is the fraction of the disintegrations resulting in the emission of the particular gamma ray. In all cases but one, the assumed target material in which the production reaction takes place is beryllium ($A_T = 9$), and for the case when the radioactive component is ^{56}Co, D_2O ($A_T = 2$) is assumed. The (γ,n) cross sections for ^{9}Be and deuterium are given in Fig. 6 as a function of the gamma-ray energy.

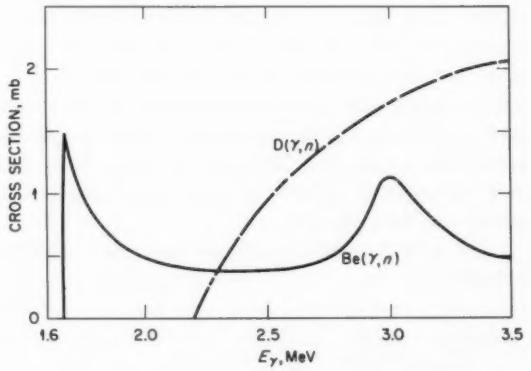

Fig. 6 The (γ,n) cross sections for beryllium and deuterium vs. gamma-ray energy.

The energy, E_n (MeV), of a neutron produced by a (γ,n) reaction in a nucleus of mass A_T is given[1] by

$$E_n = \frac{A_T - 1}{A_T}\left[E_\gamma - E_0 - \frac{E_\gamma^2}{1862(A_T - 1)}\right] + \left[\frac{2(A_T - 1)(E_\gamma - E_0)}{931 \quad A_T^3}\right]E_\gamma \cos\theta \quad (3)$$

where E_γ is the gamma-ray energy (MeV), E_0 is the threshold energy for the reaction (MeV), and θ is the production angle. The second term, which corresponds to the kinematic spread in the energy, is very small compared to the first term and will therefore be neglected.

The neutron intensity per unit activity, n, for each of these sources, the corresponding neutron energies, the yields, and the total neutron intensities resulting from such yields are indicated in Table 1, together with data for the ^{124}Sb–Be source for comparison. A striking feature of these data is the great variety of neutron energies that will be available with such sources. Also, gamma rays of a given energy produce a very sharply spiked distribution of neutrons—i.e., essentially monoenergetic. Thus, it seems that this expanded arsenal of isotopic neutron sources should prove very useful for energy-dependent applications.

Other factors important in considering such isotopic neutron sources are half-life, total specific activity, and neutron intensity. Regarding half-life, only two of the sources listed—107-day ^{88}Y and 77-day ^{56}Co—are comparable to or better than the currently used 60-day ^{124}Sb. The others are, perhaps, too short lived to be useful for wide-scale commercial applications; however, if these sources can be produced economically, they may prove feasible for more specialized applications requiring the variety of neutron energies that they offer.

The specific activity of the radionuclide used in the neutron source is important because it determines the size of the source. We estimate that the yttrium source consists of about 70% ^{88}Y nuclei, while the cobalt source consists of only about 6% ^{56}Co nuclei. The bismuth source, according to calculations, consists of about 20% ^{205}Bi and ^{206}Bi. However, since the cross sections for ^{207}Bi, ^{208}Bi, and ^{209}Bi are probably more greatly exaggerated than those for ^{205}Bi and ^{206}Bi, the specific activity of this source is likely to be much higher. All the sources listed can probably be made much smaller than the ^{124}Sb source since the latter is produced by the (n,γ) reaction in ^{123}Sb (a sealed unit is irradiated in a nuclear reactor).

Perhaps the most obviously important characteristic of any neutron source for most applications is the total neutron intensity. On this basis alone, the bismuth source would seem to be the best choice; even if, as noted earlier, the total neutron intensity recorded for this source is about an order of magnitude too high, the more realistic figure is still quite significant. The yttrium source has the best total neutron intensity of all the isotopic sources listed and, on a per-curie basis, is equal to the ^{124}Sb source. The cobalt source is comparable in strength to the bismuth source, assuming about 10^8 n/sec for the latter case.

Thus, considering the three factors stated above, the ^{88}Y–Be source is far superior to all others listed. In comparison with the currently used ^{124}Sb–Be source, the yttrium source has almost a factor-of-2 advantage in half-life, can probably be made much smaller, and is equivalent in strength on a per-curie basis. The 150-keV neutrons provided by the yttrium source are more penetrating than the 24-keV neutrons provided by the ^{124}Sb–Be source, which may be a disadvantage for some applications—e.g., thermal-neutron radiography—but may be an advantage for others—e.g., in assay systems.[9] For applications that require very high intensities ($\sim 10^{10}$ n/sec), ^{252}Cf will undoubtedly remain the best choice among isotopic neutron sources; however, for applications requiring an intermediate intensity (10^7 to 10^8 n/sec), the ^{88}Y–Be source may prove superior to any other isotopic neutron source. Recall, for example, that ^{252}Cf neutrons are characterized by a fission spectrum. A cost analysis[9] of the production of an ^{88}Y–Be source, which includes target material, chemical processing, and fabrication, indicates that the ^{88}Y–Be source is economically competitive with the ^{124}Sb–Be source. This result is due in no small measure to the fact that at the LAMPF there will be no prime-beam-time cost for producing radioisotopes. Further economies will be realized by the extraction of several desired radionuclides from a single target.

The yield of ^{88}Y presented in Table 1 is based on an irradiation time equal to the half-life of ^{88}Y—namely, 107 days. This does not seem to be the optimum production schedule for making this nuclide; rather, an irradiation time of about 1 month would be preferred, in which case about 75 Ci of ^{88}Y can be made each month, utilizing just one of the six target stations. Accounting for the beam attenuation in passing through each of the targets, the total facility capability for the production of ^{88}Y is about 240

Ci/month; however, this upper limit is unrealistic, as there will certainly be demands for other radionuclides. (MG)

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9. L. A. Kull, M. E. Schillaci, and J. R. Beyster, ^{88}Y—A New Replacement for ^{124}Sb in a Nuclear Materials Assay System, in Neutron Sources and Applications, Proceedings of the American Nuclear Society National Topical Meeting, April 19–21, 1971, Augusta, Ga., USAEC CONF-710402, Vol. III, pp. IV-94-98.

Small Irradiator*

Supplementary Keywords: *source, gamma; growth improvement; agriculture; facility description; USSR;* ^{137}*Cs.*

A small irradiator (Fig. 1) for use in presowing irradiation of seeds to accelerate seed germination and plant growth rates is manufactured by the All-Union Scientific Research Institute of Radiation Technology. The radiation source—1 Ci of ^{137}Cs arranged in two concentric circles—provides a dose whose uniformity is ±20%. The 300-cm^3 stainless-steel irradiation chamber is a short cylinder with end cones. It is mounted in a frame secured to a base and can be rotated on pivots. Although the irradiator portion of the assembly weighs about 350 kg, it can be moved by a force of only 16 kg. Seeds are introduced via a spiral channel, through which they move by gravity, and are ejected through the same channel by swinging the source assembly. The radiation dose delivered is 56 rads/hr, and about 1 kg of seeds per day can be given a 300-rad dose. The radiation dose does not exceed 0.3 mR/hr at the surface or 0.01 mR/hr at a distance of 1 m. (MG)

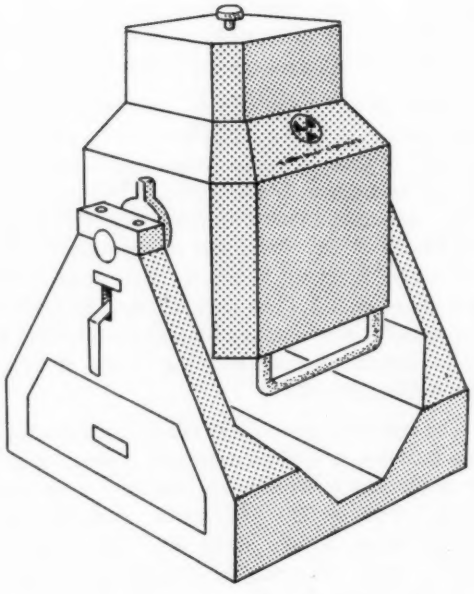

Fig. 1 Russian 1-Ci ^{137}Cs irradiator for presowing irradiation of seeds.

*A. A. Vikulin, V. M. Komonov, and N. I. Leshckinskii (in Russian), *Atomnaya Energiya*, **27**: 174-175 (1969).

Section VI

Isotopes and Radiation Technology

Applications in Life Sciences

Twenty-Five Years of Isotopes in Life Sciences

By John L. Kuranz*

Supplementary Keywords: *review, historical.*

The field of radioisotope application in life sciences has been expanded over the past 25 years by the efforts in several disciplines. George Hevesy, a chemist working with Ernest Rutherford in Manchester, England, in 1912, first demonstrated the value of a radioisotope as a research tool in the life sciences.† Assigned the task of separating radium D from lead, which was impossible by chemical methods, Hevesy familiarized himself with the properties of radioactive lead and was led to the fundamentally new step of using radioactivity as an instrument of discovery. He found that radioactive lead could be substituted in all chemical reactions for ordinary lead and, because of its radioactivity, could be followed through even the most complex chemical operations. He found also that the radioactivity could be used as a quantitative measure for lead. In 1923, at the University of Copenhagen, Hevesy again used radioactive lead, this time for tracing the metabolism of lead in bean plants, and the real value of tracer chemistry then began to become apparent. Later he used radioactive phosphorus to follow metabolism in living tissues. Since a chemist first discovered the usefulness of radioisotopes as a scientific tool and since the chemical and radiochemical purities of radioisotopes are very important in this technique, we may say that radioisotopes in the life sciences might be nonexistent without the initial discoveries and the continuing product development by chemists of various specialties.

*Amersham/Searle Corporation, 2636 South Clearbrook Drive, Arlington Heights, Ill. 60005.

†G. von Hevesy, Radioactive Tracers and Their Applications, *Isotopes and Radiation Technology*, 4(1): 9-12 (Fall 1966).

Starting in the summer of 1946, the Manhattan Engineer District (MED), which later became the AEC, through Clinton Laboratories, later ORNL, made various radioactive isotopes available and began a program to synthesize certain useful radioactive compounds for use in its research laboratories. The MED also initiated the sponsorship of industrial development of a broad line of radiochemicals, while its Divisions of Research and of Biology and Medicine and other government agencies began to give financial support to many technical programs in academic institutions throughout the United States. The acceptance of the radioisotope by life scientists took a quantum jump ahead after 1946. This was due mainly to the availability of many new isotopes and isotope-labeled compounds and, of course, to the stimulus provided by government grants to universities and development contracts to industry.

This growth is reflected in the increasing number of periodicals that print papers concerned with radioisotope uses in life sciences (Fig. 1). For the most part the growth, which exceeded 20% per year, can be attributed to (1) the fundamental usefulness of the radioisotopic technique in analysis of living systems; (2) the early interest on the part of senior investigators in the life-science community; (3) the introduction by educators of isotope technology into the life-science curriculum; and (4) the fashionability of the new technique. During the early 1950s some leading life scientists jokingly described an isotope as that material which, when introduced into a living system, produced a technical paper. This attitude did not, however, last long.

The radioisotopic technique is sometimes the tool of choice due to its high sensitivity, reproducibility, or timesaving, and sometimes it is the only tool available.

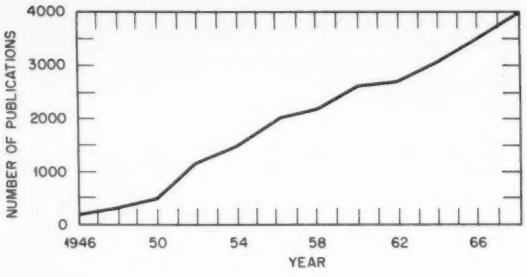

Fig. 1 Number of technical publications concerning radioisotopes in life sciences. The figures do not include the thousands of rather routine applications of ^{14}C and ^{3}H or any of the numerous isotope applications in clinical medicine.

The following description of a typical analytical radioisotope application in living systems illustrates the unusual characteristic of the radioisotope as an analytical tool and suggests some of the special challenges it presents.

Assume that a scientist wishes to evaluate adrenal function by measuring the cortisol content in human plasma using an isotope-dilution technique. The normal concentration of cortisol in plasma is only 10 μg per 100 ml. An analysis performed on 2 ml of plasma would therefore be dealing with only 0.2 μg of cortisol. If 0.5 nCi (equivalent to 1000 disintegrations/min) of radioactive cortisol is required initially for determination of the steroid, the analyst would actually be adding about 0.004 μg of a singly ^{14}C-labeled material (at low specific activity) to his sample. For a steroid containing two hydrogens replaced by tritium, only 5 $\mu\mu$g of radioactive material needs to be used. Yet, these quantities can be accurately ascertained to ±3% by commercially available counting equipment using standard techniques.

The use of a labeled precursor in the biosynthesis of a natural product is another good example, e.g., biosynthesis of steroids from mevalonic acid. Equally important has been the use of labeled substrates in the study of the citric acid cycle.

The synthetic organic chemist has also played a significant role in the development and success of important radioisotope applications. The production of complex organic radiochemicals at extremely high specific activity involves reactions on a 10- to 100-mg scale and has necessitated the development of microtechniques. To ensure radiological safety, it may be necessary for the reactions to be carried out behind protective shielding, and this involves specially designed apparatus, remotely controlled. Also, sensitive microtechniques have had to be devised for the purification and characterization of radioactive products. Procedures such as paper chromatography, usually used just for analysis, are frequently used for the purification of radiochemicals.

Biological production methods, e.g., enzymatic syntheses, are becoming increasingly important, and consequently the biochemist is now playing a greater role in the development of the radiochemical industry. The most important requirement for a radiochemical used in a biological tracer experiment is a high radiochemical purity. High specific activity and high chemical purity are also needed in some applications, chemical purity being more significant in chemical investigations. A preparation of alanine-1-^{14}C containing 10% of the activity as glycine-1-^{14}C has a radiochemical purity of 90%. Tenfold dilution of this mixture with pure nonradioactive alanine will increase the chemical purity to 99% but will leave the radiochemical purity unchanged at 90%. Most radiochemicals now available have radiochemical purities of at least 95%. Some enzyme assays in which there is only 2% conversion of the radiochemical used as substrate require labeled compounds with radiochemical purities greater than 99%.

The packaging of small amounts of high-specific-activity materials creates other problems for the manufacturer of radiochemicals. The smallest ^{14}C package size (10 μCi) of steroid mentioned above contains only 72 μg of product, while the tritium compound (250 μCi) contains only 3 μg of product. Thus the problem of what would normally be considered trace impurities in containers or solvents used in packaging may, in fact, amount to more material than the product itself. One can also appreciate the problem of a few bacteria in a package containing 3 μg of a labeled amino acid.

In addition, users and suppliers need to be aware of the radiation decomposition that can occur with labeled compounds, i.e., decomposition of compound by the radiation emitted, which produces radiochemical impurities. However, much information has now been accumulated on the optimum condition for storing labeled compounds.

Figure 2 shows the dollar growth in the use of radioisotopes and associated equipment in the life sciences. This somewhat tracks the shape of the previous chart, but we should not conclude that most life-science applications as summarized in this figure involve completely new techniques. Much of the last 5 years' usage includes applications of techniques developed during the late 1950s and early 1960s.

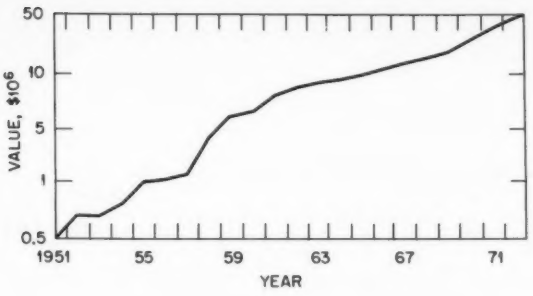

Fig. 2 Use of isotopes and related equipment in life sciences.

The growth of radioisotope use in the life sciences over the past 25 years has, indeed, been notable. The next 25 years should witness at least the same rate of expansion of the isotope as an important tool for the life scientist. Analytical chemistry could, from a technical standpoint, make the radioisotope as useful to its endeavors as has biology and biochemistry. Even though the radioisotope was introduced by the chemist to the biologist, the analytical chemist has not yet made the extensive use of this new tool in his laboratories as has the life scientist. This should present an interesting challenge to the analytical chemist.

(MG)

Role of ^{32}P and ^{33}P in the Synthesis of a Gene*

Supplementary Keywords: *biochemistry; biology; chemistry, organic; material tracing; reaction mechanism; molecular structure; multiple tracing; chromatography; kinetics.*

A gene has been synthesized from its constituent nucleotides! It is a yeast alanine tRNA gene—a relatively simple one that contains only 77 nucleotides. But the synthesis of this simple gene is exceedingly complex. This feat of technical ingenuity was accomplished by H. G. Khorana and a team of associates at the Institute for Enzyme Research of the University of Wisconsin. The total plan for the synthesis is shown in Fig. 1; the steps in the blockwise synthesis of segment 6 of the 17 segments (shown by brackets in Fig. 1) are diagrammed in Fig. 2. From commercially available nucleotides, the single segments were built up by chemically blocking off all but the requisite active sites; each segment contained 8 to 20 nucleotides. The segments were then joined in such a way as to form the three large double-stranded parts of gene material (A, B, and C of Fig. 1). Segments on the same strand were bonded with DNA ligase. The strands were bound together by the natural attraction of genes on complementary strands. Finally, the three large parts were joined to produce the synthetic gene; total synthesis was achieved in each of two ways: by joining preformed (B + C) to A and by joining preformed (A + B) to C.

The radioisotopes ^{32}P and ^{33}P were used extensively throughout the synthesis. Their roles were to ensure that the nucleotides had combined in the correct order, to establish the kinetics of the joining reactions, to characterize the joined products (segments and parts), and to check the purities of the products. Khorana describes the use of these radionuclides in the gene synthesis as follows:

> Characterization of the joined products was aided by manipulation of the specific activity of γ-^{32}P-ATP used in phosphorylation reactions. Thus, radioactivity at the internal linkage points in A, B and C was much weaker than that used at the termini which were to connect A to B and B to C. Further, in multiple joinings (for example, in C), stoichiometry of the joining of different segments was promoted by the concomitant use of ^{32}P and ^{33}P isotopes. Stoichiometric joining of A to B and B to C was similarly confirmed by using highly radioactive ^{32}P at the 5′-termini in B while the appropriate 5′-termini in A and C contained highly radioactive ^{33}P.

Since nucleotide-by-nucleotide gene synthesis has been so successfully demonstrated, the synthesis of other genes—including those which do not occur naturally—is expected soon to follow. This major advance in molecular biology will undoubtedly bring a better understanding of the molecular basis of life and thus help to overcome genetic diseases or to create desirable mutants.

(HPR)

*From K. L. Agarwal, H. Büchi, M. H. Caruthers, N. Gupta, H. G. Khorana, K. Kleppe, A. Kumar, E. Ohtsuka, U. L. Rajbhandary, J. H. Van de Sande, V. Sgaramella, H. Weber, and T. Yamada, Total Synthesis of the Gene for an Alanine Transfer Ribonucleic Acid from Yeast, *Nature*, **227**: 27-34 (1970), and Biodesign with Man-Made Genes?, *Industrial Research*, **12**(8): 24 (1970).

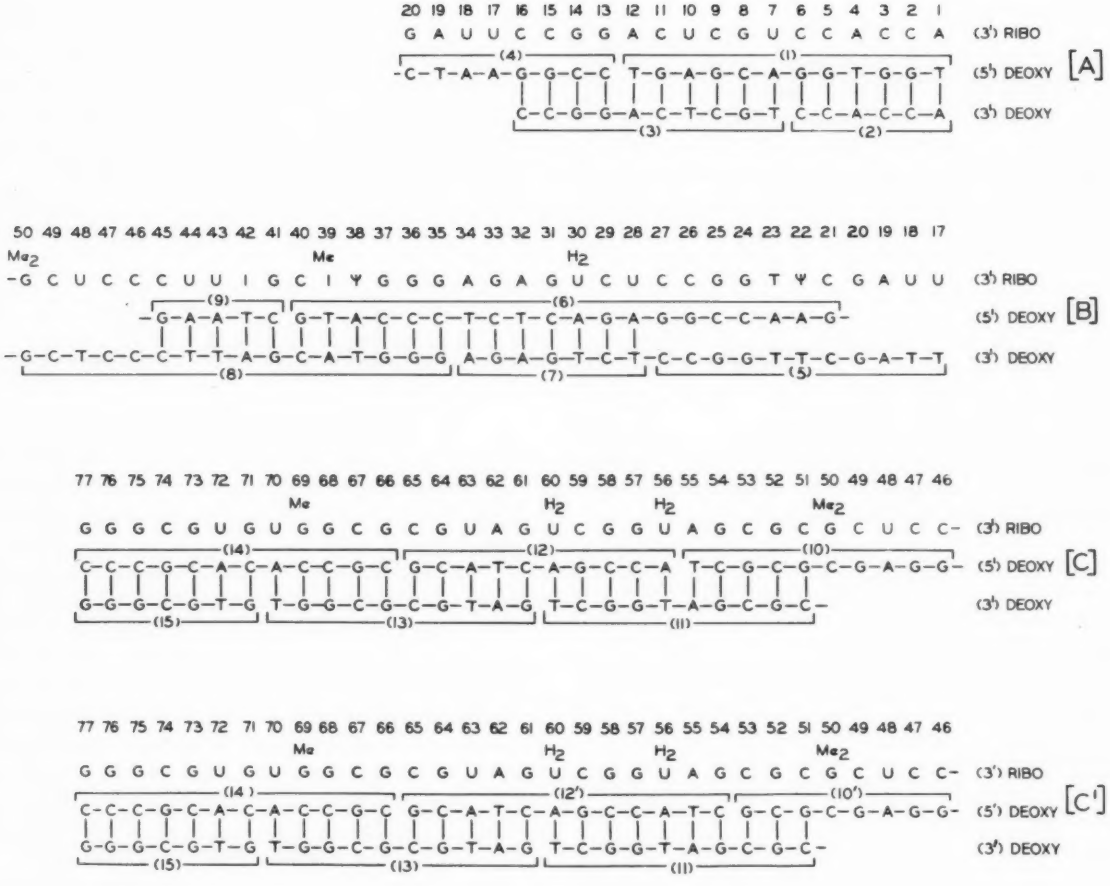

Fig. 1 Total plan for the synthesis of a yeast alanine tRNA gene. The chemically synthesized segments are in brackets, the serial number of the segment being shown within the brackets. Seventeen segments (including 10' and 12') varying in chain length from penta to icosanucleotides were synthesized. In the syntheses, the assumption was made that the rare bases present in the tRNA arise by subsequent modification of the four standard bases used by the transcribing enzyme. Thus inosine is formed by deamination of adenosine and so comes from an A · T base-pair in DNA. [From *Nature*, 227: 27-34 (1970), with permission.]

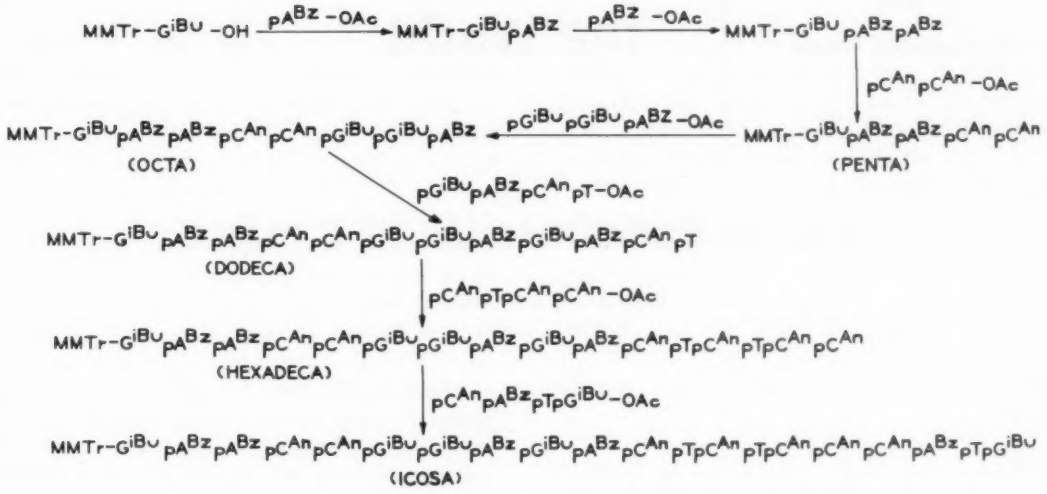
MMTr-GiBu -OH
pABz -OAc
MMTr-GiBu pABz
pABz -OAc
MMTr-GiBu pABz pABz
pCAn pCAn -OAc
MMTr-GiBu pABz pABz pCAn pCAn
(PENTA)
pGiBu pGiBu pABz -OAc
MMTr-GiBu pABz pABz pCAn pCAn pGiBu pGiBu pABz
(OCTA)
pGiBu pABz pCAn pT-OAc
MMTr-GiBu pABz pABz pCAn pCAn pGiBu pGiBu pABz pGiBu pABz pCAn pT
(DODECA)
pCAn pTpCAn pCAn -OAc
MMTr-GiBu pABz pABz pCAn pCAn pGiBu pGiBu pABz pGiBu pABz pCAn pTpCAn pTpCAn pCAn
(HEXADECA)
pCAn pABz pTpGiBu-OAc
MMTr-GiBu pABz pABz pCAn pCAn pGiBu pGiBu pABz pGiBu pABz pCAn pTpCAn pTpCAn pCAn pCAn pABz pTpGiBu
(ICOSA)

Fig. 2 Steps in the blockwise chemical synthesis of an icosadeoxyribonucleotide. The standard method of presentation of polynucleotide chains is used, with the letter p to the left of a nucleoside symbol indicating a 5′-phosphate and to the right indicating a 3′-phosphate. MMTr indicates a monomethoxytrityl group present at the 5′-hydroxyl end of the terminal nucleoside. The protecting groups on the heterocyclic rings of different deoxyribonucleosides are shown by superscripts on the nucleoside initials: An, anisoyl; Bz, benzoyl; iBu, isobutyryl; OAc at the right-hand end of oligonucleotides stands for 3′-O-acetyl. [From *Nature*, 227: 27-34 (1970), with permission.]

Section VII

Isotopes and Radiation Technology

Isotopes Around the World

Use of Radioisotopes in Canada*

Summarized by Martha Gerrard

Supplementary Keywords: *economics; industry; medicine; education.*

A survey of the use of radioisotopes by Canadian industry, prepared in 1969 (from mid-1968 data), was released in 1970. Because of the time required to analyze the data obtained in such a survey, the final report is inevitably out of date before it is issued. However, because so few industrial surveys have been published, the Canadian report is summarized here. Details are available in the original report.

The Canadian group compared its results with Japanese data published annually† and with data from an IAEA worldwide survey‡ published in 1965—the only extensive surveys publicly available.

The Canadian survey data showed that radioisotope use in medicine, research, and education in Canada had kept pace with that in other countries, but industrial applications had not reached their full potential. Apart from gaging, industrial applications were limited, and even the gaging equipment was mostly imported—only one Canadian manufacturer was identified as a primary producer of this equipment.

Radioisotopic gages are used in Canada for measuring thickness, density, liquid level, moisture, and dew point. Other devices are used for sensing in fire-alarm systems and for ionizing air to eliminate static electricity. Of the 1238 gages reported—a slight increase over the 1155 reported in 1963—more than half were for measuring density. The gages are being used in the various types of production and service industries as well as in academic research. The 1238 compares with 1776 in Japan in 1968 and with 2006 in the United Kingdom in 1963. The Canadian survey revealed no snow gages, compared to 12 in Japan, or sulfur-determination instruments, compared to 59 in Japan. In addition, 801 ionization gages were reported, 688 of which were in use as fire alarms and 73 as static eliminators. These numbers show a decline in the use of these two devices from 2814 and 1022, respectively, since 1963.

The average installation cost per gage and the maintenance cost per year per gage were estimated as

	Installation	Maintenance
Food industry	$2200	$300
Tobacco industry	5000	750
Wood and paper industry	4140*	500
Chemical industry	4200*	200
Ceramics industry	5600	300
Petroleum and coal industry	4000*	500
Metals industry	3000	300
Machine industry	2700*	150
Service industries	3000	750

*With an installation that includes feedback mechanisms for process control, the cost is two to three times that given.

*Summary of a 1969 report prepared for the Canadian Nuclear Association and sponsored by the Radioisotopes Committee of the Association.

†For example, Japan Radioisotope Association, *Statistics of Radiation Use in Japan—1968* [summarized in *Isotopes and Radiation Technology*, 7(1): 121-123 (Fall 1969)].

‡*Industrial Radioisotope Economics*, Findings of Study Group Meeting, Vienna, 1964, International Atomic Energy Agency, Vienna, 1965 (STI/DOC/10/40) [summarized in *Isotopes and Radiation Technology*, 3(2): 152-166 (Winter 1965–1966)].

Although Canada has been a leader in producing very-high-activity radioisotopic sources for massive irradiation in industrial processes and has supplied many specially designed irradiators to other countries, large-scale-radiation application in Canada has been negligible in food processing and very limited in sterilization of medical products—yet the greatest potential demand for radioactive isotopes is considered to be in massive irradiation applications. Fifty-six irradiators—51 containing ^{60}Co and 5 containing ^{137}Cs—were reported to be in use—44 for general research, 7 for academic research, 4 for medical research, and only 1 for industrial production (although two pilot-scale irradiators were reported). This count put Canada in about a median position in the worldwide picture of industrial irradiation. Such varied materials as wheat leaves, glass, plastics, silicon semiconductors, corn-borer larvae, meat, whitefish, dried-egg products, fresh eggs, milk, potato and apple slices, frozen beefsteak, textile fibers, rye, wheat and barley seed, mushrooms, cuttings of various plant materials, fungal spores with radiosensitizers, potato tubers, rolled oats, and aortic hemografts are being irradiated. Canada reported 30 irradiators in the 1963 IAEA survey.

Teletherapy sources, which include kilocurie amounts of both ^{60}Co and ^{137}Cs, account for by far the largest amounts of radioisotopes used in medicine. Of the world's 2400 teletherapy units containing a thousand or more curies of radioactivity each, 49 were in Canada at the time of the survey. The activities of such units ranged from 1400 to 9700 Ci, averaging 4500 Ci, and radioisotope costs averaged more than $25 thousand per unit.

Survey returns on gamma radiography indicated that 10 service companies were using 18 ^{192}Ir sources (1185 Ci) and 2 were using ^{60}Co sources (45 Ci) for gamma radiography. A considerably greater curiage is in use for in-house gamma radiography.

The 10 most widely used isotopes and the approximate amounts of each used were reported as

Isotope	Annual use, Ci	Isotope	Annual use, Ci
^{60}Co	1,146,000	^{99}Mo (^{99m}Tc)	34.3
^{137}Cs	12,720	^{85}Kr	26.5
^{3}H	2,022	^{131}I	23.9
^{192}Ir	1,525	^{32}P	12.9
^{241}Am	173	^{133}Xe	12.0

Smaller amounts of all the common isotopes were reported used in education, medical diagnosis, and brachytherapy. (MG)

Section

VIII

Isotopes and Radiation Technology

Miscellaneous

Availability of Isotopes and Services

AEC PROPOSES TO WITHDRAW FROM PRODUCTION OF 28 RADIOISOTOPES

The USAEC has turned over to private industry all production and distribution of 28 reactor-produced radioisotopes. These are in addition to the 37 radioisotopes whose production by the AEC has gradually been discontinued since 1961, in keeping with its policy of withdrawing from areas where commercial firms have demonstrated ability to meet market needs.

The additional 28 products, which are used principally for research and development and medical applications, were formerly available commercially as well as from AEC's Oak Ridge National Laboratory at Oak Ridge, Tenn. The Commission has determined that there is adequate private capability for their production, that effective competition in marketing exists, and that commercial prices are reasonable. The 28 radioisotopes are: ^{122}Sb, ^{131}Ba, ^{133}Ba, ^{210}Bi, ^{14}C, ^{131}Cs, ^{36}Cl, ^{67}Cu, ^{72}Ga, ^{130}I, ^{194}Ir, ^{63}Ni, ^{191}Os, ^{109}Pd, ^{142}Pr, ^{186}Re, ^{86}Rb, ^{153}Sm, ^{46}Sc, ^{111}Ag, ^{182}Ta, ^{125m}Te, ^{204}Tl, ^{170}Tm, ^{171}Tm, ^{185}W, ^{187}W, and ^{188}W.

During fiscal year 1970, AEC's sales of these products totaled about $114,000 and represented about 16 Ci. Oak Ridge National Laboratory would continue to distribute other radioactive items not yet available from commercial sources.

AECL PREEMPTS ^{60}Co MARKET

With the obtaining of its twenty-first industrial-irradiator order, Atomic Energy of Canada Limited, which already dominates the ^{60}Co teletherapy-unit market, now is the leader in industrial-irradiator sales. A general-purpose facility has recently been installed for Radiation Technology, Inc., at Rockaway, N. J., with an initial loading of 250 kCi. A full-scale (initial loading 50-kCi) facility was installed for the South Africa Atomic Energy Board for operation at Pelindaba; one in Yavne, Israel, for Sorvan Irradiation Limited (35 kCi); and one in Melbourne, Australia (200 kCi). The ultimate capacity of all these irradiators is more than a million curies. By 1975 the Pickering nuclear station outside Toronto will be able to provide more than 12 million Ci of ^{60}Co annually for industrial applications. Details on two of the facilities have not been released. The other 19 are:

1. Ethicon, Peterborough, Ontario, Canada
2. Ethicon, Somerville, N. J., USA
3. Ethicon, San Angelo, Tex., USA
4. Tasman Vaccine, Upper Hutt, New Zealand

5, 6. India Department of Atomic Energy, Trombay, India

7. Firma Wili Rusch, West Germany
8. Ethicon Spa, Rome, Italy
9. NUNC A/S, Roskilde, Denmark
10. Becton & Dickenson, Connecticut, USA
11. RTI, St. Hilaire, Quebec, Canada
12. RTI, Rockaway, N. J., USA
13. Gammaster, Utrecht, Netherlands
14. Novo, Denmark (March 1971)
15. Kobo (Textile Institee), Czechoslavakia (April 1971)
16. Johnson & Johnson, Rotbro, Sweden (September 1971)
17. South Africa Atomic Energy Board, Pelindaba, South Africa (May 1971)
18. Sorvan Irradiation, Yavne, Israel (July 1971)
19. Tasman Vaccine, Melbourne, Australia (July 1971)

RADIOISOTOPIC RADIOGRAPHY UNITS

Two portable radiography units (Fig. 1), the Century and the Gamma 35, weighing 32 and 25 lb, respectively, are being marketed by Gamma Industries (P. O. Box 2543, Baton Rouge, La. 70821). The Century source is 100 Ci of ^{192}Ir and can be inserted in the 35-Ci Gamma 35 unit when decay has made it no longer satisfactory for the larger unit. The depleted

uranium shields are enclosed in polyurethane, which acts as a cushion in case the unit is dropped. The quick-disconnect couplings used instead of threaded ones are reusable. Another portable 100-Ci ^{192}Ir radiography unit, the Pipeliner Model-1, also weighing 35 lb, is especially designed to be moved along a pipeline.

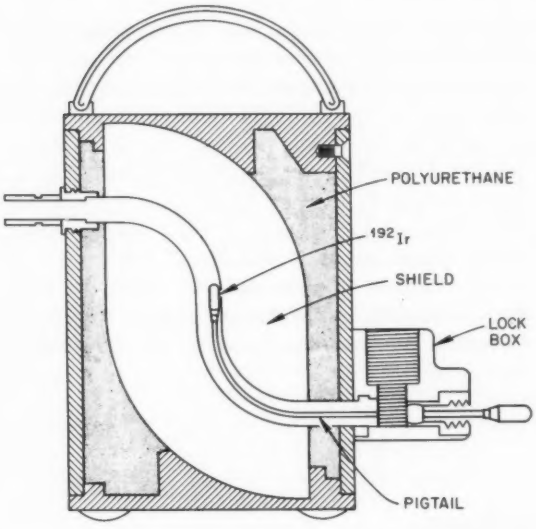

Fig. 1 Portable radiography source using ^{192}Ir.

The Gammatron 100, containing 100 Ci of ^{60}Co and weighing 450 lb, can be mounted on wheels. It also has a depleted uranium shield and a polyurethane cushion. A model with 200 Ci is a fixed unit, while the Gammatron 10, with a 10-Ci source, weighs 150 lb and can be carried by two men.

The Utility Twin model contains 20, 50, or 100 Ci of ^{60}Co (825, 945, or 1300 lb) and can be mounted on wheels. The ^{60}Co can be replaced by ^{192}Ir.

RADIATION DYNAMICS TO SELL VICKERS PRODUCTS

Radiation Dynamics Inc. (RDI), Westbury, N. Y., is handling the marketing, sales, service, and maintenance of Vickers' radiation and nuclear engineering division products in the United States, Canada, and Mexico while Vickers is doing the same for RDI products in Britain. Vickers products include linear accelerators for medical purposes, industrial radiography, and industrial processing and ^{60}Co irradiation facilities. RDI, a Firestone Tire and Rubber Company group, claims to offer the world's widest range of commercial radiation equipment for industrial processing and medical therapy.

NEW RADIOCHEMICAL CENTRE CATALOG

The 1971 edition of the Radiochemical Centre's catalog describes a comprehensive range of radioactive products for all purposes and includes many new developments. It is in four separate parts:

Radiopharmaceuticals and Clinical Radiation Sources for hospital and medical research use.

Radiochemicals for other tracer uses.

Radiation Sources for Industry and Research for process control, nondestructive testing, and gamma-radiation processing use.

Radioactivity Standards for instrument calibration use.

New to the catalog are the sterile technetium and strontium generators, two new types of clinical sources for bone densitometry, and an increased range of ^{137}Cs tubular and spherical sources. The Centre offers more than 1400 chemicals—including labeled amino acids, nucleic acids, steroids, and carbohydrates—incorporating 150 different radionuclides. Several hundred types of radiation sources are available, including the recently introduced ^{242}Cm alpha foils, ^{85}Kr, beta point sources, and a new design of ^{241}Am line source. The standards catalog shows a full range of absolute and reference standards.

Copies are available from The Radiochemical Centre, Amersham, Bucks., England.

HIGH-PURITY GERMANIUM DETECTORS

Dr. Fred Goulding of Berkeley, under contract to the Bureau of Mines, is investigating detector capability for a number of applications, including X-ray fluorescence for environmental problems. He reports that the manufacture of detectors from high-purity germanium is very simple, but the cost of growing the material is significant.

A unit for brain scanning, comprising 144 high-purity germanium detectors, has been constructed by the General Electric group at Valley Forge and delivered to New York University Medical School for evaluation. The isotope used is ^{133}Xe.

A photon spectrometer that incorporates a high-purity germanium detector is being marketed by General Electric Company, Space Technology Products

(P. O. Box 8439, Philadelphia, Pa. 19101). The instrument withstands extended room-temperature storage and even repeated thermal cycling and has a resolution superior to that of similar available instruments over a wide photon-energy range. The unique detector construction employed results in thin window–high efficiency for the low-energy X rays of all elements.

ISOTOPE PRODUCTS LABORATORIES ANNOUNCES X-RAY-FLUORESCENCE SOURCES

Isotope Products Laboratories, 404 South Lake Street, Burbank, Calif., is offering for sale a number of annular sources that are suitable for X-ray-fluorescence spectroscopy. Sources of ^{241}Am, ^{55}Fe, ^{109}Cd, and ^{57}Co are available in source strengths of 5 to 50 mCi and with various types of encapsulation.

The same company is also offering two types of ^{252}Cf sources. One of these sources is left uncovered to provide a source of fission fragments and alpha particles. The other is sealed in an aluminum capsule to prevent escape of fission products and is designed to provide a point source of neutrons.

Isotope Products also sells a line of $^{90}SrTiO_3$ sources that are suitable for a wide range of industrial applications such as gaging.

COURSES IN RADIOISOTOPIC TECHNIQUES

Several courses announced by Oak Ridge Associated Universities, under sponsorship of the U. S. Atomic Energy Commission, are: Environmental Assessment, Nov. 8–19, 1971; Environmental Aspects of Radiation Sciences, Jan. 24–Feb. 11, 1972; Radioisotopes in Research, Apr. 3–28, 1972; Health Physics and Radiation Protection, Apr. 3–June 9, 1972; Nuclear Medical Technology, Apr. 10–May 5, 1972; Medical Radioisotopes, May 8–June 2, 1972.

Information may be obtained from Dr. L. K. Akers, Chairman, Special Training Division, Oak Ridge Associated Universities, P. O. Box 117, Oak Ridge, Tenn. 37830.

AEC Activities

ORNL HIGHLIGHTS OF THE 1960s

1960	Multikilocurie amounts of ^{85}Kr were purified at ORNL.
1960	Kilocurie quantities of ^{147}Pm were purified at ORNL.
1960	Multikilocurie quantities of ^{144}Ce were purified at ORNL.
May 1961	The Weather Bureau thermoelectric generator sponsored jointly by the U. S. Weather Bureau and the AEC's Division of Isotopes Development was fueled at ORNL with 17 kCi of strontium titanate.
August 1961	SNAP-7C was fueled at ORNL with 40 kCi of strontium titanate.
September 1961	SNAP-7A was fueled at ORNL with 40 kCi of strontium titanate.
1962	Xenon-133 was first separated at ORNL for distribution.
1962	Liquid–liquid extraction techniques were demonstrated on a plant scale for ^{147}Pm and ^{90}Sr.
1962	Two-stage differential solvent extraction process was developed and demonstrated at ORNL's Fission Products Development Laboratory. Although evaluated by separating and recovering uranium from spent homogeneous reactor fuel, it can also be used to separate useful radioisotopes from the fission-product mixture.
January 1962	The Isotopes Development Center was established at ORNL.
March 1962	SNAP-7E was fueled at ORNL with 30 kCi of strontium titanate.
May 1962	SNAP-7D was fueled at ORNL with 224 kCi of strontium titanate.
July 1962	ORNL began a sealed-source safety-evaluation program. This program resulted in the AEC–ORNL source-capsule classification system in 1967 and a source-application guide in 1969.
1963	A method of shipping multikilocurie quantities of ^{137}Cs adsorbed on zeolite was developed at ORNL.
1963	Building 3047 was constructed at ORNL. This is the high-radiation-level research and development facility.
April 1963	The First Oak Ridge Radioisotope Conference, sponsored by ORNL, ORAU, and AEC, was held in Gatlinburg, Tenn.

November 1963	The Graphite Reactor at ORNL was shut down. This reactor was later (September 1966) dedicated as a National Historic Landmark and opened to the public.
1964	The technique for pelletizing ^{90}Sr titanate by remote hot pressing of the powder in a hot cell was developed at ORNL.
1964	An air-pulsed mixer–settler for remote operation was developed at ORNL.
1964	ORNL produced ^{14}C having an assay of 92% ^{14}C. This is the highest specific activity ^{14}C made to date.
April 1964	The Second Oak Ridge Radioisotope Conference, sponsored by ORNL, ORAU, and AEC, was held in Gatlinburg, Tenn.
April 1964	ORNL and the Marquardt Corp. conducted the first demonstration of a ^{60}Co heated space thrustor using hydrogen propellant.
June 1964	AEC sponsored a meeting at Germantown to discuss isotope-production technology with industrial representatives. At this meeting, manuals of isotope-production methods at ORNL, BNL, Mound Laboratory, and Savannah River were given to the participants.
September 1964	ORNL and RCA ran a joint test on a new type space generator that had been developed at RCA and fueled with 100 kCi of strontium titanate.
1965	A 10-year-old ^{137}Cs teletherapy source was returned to ORNL and was examined for possible corrosion. No corrosion was found.
March 1965	ORNL began enrichment of ^{85}Kr by thermal diffusion.
1966	The Radioisotope Sand Tracer (RIST) study, a cooperative program of ORNL and a number of state and federal agencies, was begun.
1966	The first multigram quantities of ^{242}Cm were produced and separated at ORNL.
March 1966	The Isotopes Information Center at ORNL was formally announced.
October 1966	ORNL and the Martin Company successfully completed a 90-day test of SNAP-11 under simulated lunar day and night conditions. This generator was powered by 25 kCi of ^{242}Cm.
1967	Iodine-123 was made available at ORNL.
February 1967	AEC and the Southern Interstate Nuclear Board sponsored a meeting on the radiation preservation of foods. ORNL cohosted the meeting.
March 1967	ORNL and the U. S. Department of Agriculture announced the development of a nuclear gage to measure the strength of egg shells.
July 1967	A new ORNL catalog was issued which listed the following new and experimental products: ^{39}Ar, ^{74}As, ^{109}Cd (from silver target), ^{141}Ce, ^{131}Cs, ^{60}Co (carrier free), ^{67}Cu, ^{71}Ge, ^{59}Fe (carrier free), ^{79}Kr, ^{33}P, ^{43}K, ^{188}Re, $^{121m,121}Te$, ^{123m}Te, ^{125m}Te, ^{171}Tm, ^{188}W, ^{131m}Xe, ^{69m}Zn.
1968	ORNL produced strontium silicate beta sources. These sources are strontium silicate embedded in an aluminum matrix.
1968	SNAP-21 was fueled at ORNL with 30 kCi of strontium titanate for use in deep-sea systems.
1968	SNAP-23 was fueled at ORNL with 165 kCi of strontium titanate. This was the largest ^{90}Sr capsule ever assembled.
1968	ORNL initiated fueling services for commercially manufactured thermoelectric generators.
1968	ORNL fabricated radioactive ^{152}Eu metal target for cross-section measurements.
October 1968	The Second International Symposium on Packaging and Transportation of Radioactive Materials was held at Gatlinburg, Tenn. The AEC and ORNL were cosponsors.
October 1968	The Low Intensity Testing Reactor, the first reactor to make high-specific-activity isotopes, was shut down at ORNL.
1969	Carrier-free ^{67}Ga was produced at ORNL and tested for medical application at ORAU.
1969	Production methods for ^{153}Gd were developed at ORNL.
1969	Indium-111 was made available for medical-application testing.
1969	Four additional SNAP-21 thermoelectric generators were fueled at ORNL.
April 1969	The Third Isotopes Application Conference, sponsored by ORNL, ORAU, and AEC, was held in Gatlinburg, Tenn.
May 1969	ORNL developed and announced a new and faster solvent extraction process for separating ^{99}Mo from fissioned ^{235}U.
May 1969	The AEC Division of Isotopes Development–Weather Bureau generator was brought back to ORNL for examination, and, after it was found to be operating properly, it was fitted out for display purposes at ORNL.
November 1969	ORNL assisted the Navy in recovery of SNAP-7E generator after 7 years at 17,000 ft in the ocean.
January 1970	Radioactive ^{85}Kr of greater than 90% isotopic purity was produced by electromagnetic separation.
February 1970	First ^{244}Cm heat source (1 kW) was fabricated at ORNL.
June 1970	A meeting on radioisotope production technology, sponsored by the AEC Division of Isotopes Development and the Atomic Industrial Forum, was held at Oak Ridge to give industry the latest developments in isotope production at ORNL and other AEC sites.

General

INCREASE IN RADIOISOTOPE USES IN 1970

According to the Atomic Industrial Forum, nonpower uses of radioisotopes increased significantly in 1970. For example, radiopharmaceutical sales increased 25%, to a total of $39 million, and industrial uses of radiochemicals increased more than 10%, to a total of $25 million. In medicine, radioisotopes were used for diagnosis or therapy in 8 million patients.

AIR IONIZATION INCREASED WITH ^{241}Am

An instrument designed to supplement conventional air conditioning has been patented by Energie Froide International S.A. of Geneva, Switzerland. The ionization is produced by a ^{241}Am source. The larger proportion of negative ions is reported to improve biological well-being and to reduce the amount of pollutants in the air.

ARTIFICIAL HEART EVALUATION

Nine companies have indicated an interest in evaluating the practicability of a radioisotopic thermal converter for an artificial heart device and development of the heat source. The two phases of the project would last 7 and 17 months, respectively. Companies indicating an interest were Anatole J. Sipin Company, New York City; General Electric, Philadelphia; Hughes Aircraft, Culver City, Calif.; McDonnell-Douglas Astronautics Corp., Richland, Wash.; Nuclear Materials & Equipment Corp. (NUMEC), Apollo, Pa.; Sanders Associates, Nashua, N. H.; Trans Computer Associates, Beverly Hills, Calif.; TRW Systems Group, Redondo Beach, Calif.; and Westinghouse, Pittsburgh.

RADIOISOTOPIC HEART DEVICES

A $243,900 contract for research leading to development of an energy system weighing < 4 lb, which may be contained in and integrated into an implanted artificial heart, has been awarded to NUMEC by the National Heart and Lung Institute. The system is to use radioisotopic heat to power both a thermoelectric converter and a tiny steam engine to operate an artificial heart.

NUMEC EXTENDS NUCLEAR PACEMAKER LIFE BY GETTER-PRODUCED VACUUM

To achieve a 10-year life, which is theoretically possible, of a nuclear-powered cardiac pacemaker, a vacuum of 0.1 μ Hg is necessary. Engineers at NUMEC, a company active in development of such pacemakers [*Isotopes and Radiation Technology*, 7(2): 192-193 (Winter 1969–1970)], have found that a 50-mg pellet of Cer-Alloy 400, a getter material made by Radiation Machinery Corp., placed on each end of the radioisotopic source in the pacemaker will keep the pressure at 0.1 μ Hg.

BRITISH LIGHTHOUSE TO USE RADIOISOTOPIC GENERATOR

The UKAEA will make a 33-W Ripple (Radioisotope-Powered Prolonged Life Equipment) generator for lighthouse use. The ^{90}Sr heat source will probably be installed at a site in Ireland in 1972. A 1-W source has been used satisfactorily for 4 years to power a warning light at a water inlet to a power station.

MEETING ON MEDICAL APPLICATIONS OF SEMICONDUCTORS

A meeting on Feb. 12–13, 1971, sponsored by Dr. Paul Hoffer, Argonne Cancer Research Hospital, was attended by 280 people interested in semiconductors and detectors in general for medical applications. Interest was strong in detectors of high-Z metals.

ASTRONAUTS TAKE IRRADIATED FOOD TO THE MOON

Slices of bread like Grandma used to make accompanied U. S. astronauts on space flights Apollo 14 and 15; but these slices of bread were made from irradiated flour, and pushbuttons—not Grandma—controlled their preparation. The flour was irradiated with a ^{60}Co unit at the University of Nebraska under the supervision of Dr. Burt Maxcy; the bread was prepared by Pepperidge Farms, Inc., Connecticut, and returned to Nebraska for a second dose of radiation. The bread, packaged in individual slices, will keep up to 18 weeks at room temperature. Only a low dose of radiation is used.

Dr. Maxcy points out that use of a low dose bypasses the problems of changes in odor and texture caused by the high doses usually used by the military. The irradiated bread is judged to be fresher, less dehydrated, and better tasting than control samples. The process has possible applications for vending-machine operators, caterers, and processors of prepackaged bakery products. According to Dr. Maxcy, the USSR has already used irradiated food on several space flights. There exists a strong need for foods with extremely long shelf lives in the Skylab space program, which will involve year-long flights.

SYMPOSIUM ON THE ASSESSMENT OF RADIOACTIVE ORGAN AND BODY BURDENS

The International Atomic Energy Agency and the World Health Organization will cosponsor a symposium in Stockholm, Sweden, Nov. 22–26, 1971, concerned with the estimation of internal radioactive contamination by direct methods such as whole- and partial-body monitoring and by indirect methods such as the monitoring of excreta and body fluids. This subject matter was last dealt with comprehensively in a symposium organized by the IAEA in collaboration with WHO and the International Labor Organization in May 1964 (Symposium on the Assessment of Radioactive Body Burdens in Man, IAEA/ILO/WHO, Heidelberg, Federal Republic of Germany, May 11–16, 1964). Papers are expected to be presented on direct and indirect measurement of organ and body burdens, both total and specific radioisotopes, and interpretation of results.

SOIL–PLANT RELATIONSHIPS AND FORESTRY TO BE EMPHASIZED AT IAEA/FAO CONFERENCE

A symposium on the use of isotopes and radiation in research on soil–plant relationships, including applications in forestry, will be sponsored by the International Atomic Energy Agency (IAEA) and the Food and Agriculture Organization (FAO) of the United Nations in Vienna on Dec. 13–17, 1971. The last symposium on this subject was held in 1966. Attention will be focused on research on those physical and chemical properties of soil which influence plant growth, on uptake and translocation of nutrients by plants, and on fertilizer usage, irrigation, and other soil-management practices that increase crop production. Special sessions will be devoted to physics and chemistry of forest soils and to the nutrition, water requirements, and fertilization of forest trees.

NUCLEAR MEDICINE CONFERENCE SET

The thirteenth conference in the Oak Ridge Associated Universities nuclear medicine series, in cooperation with the AEC, will be held in Oak Ridge, Nov. 15–19, 1971. For the first time, the American College of Physicians will join in presenting the program. Thirty-five speakers are expected to present papers on medical applications of radioactive isotopes. Both papers and discussions will be directed toward the practicing physician, to help him evaluate the usefulness of diagnostic methods using radioisotopes as compared with radiologic techniques and other laboratory tests.

Abstracts of Recent Literature

Study of Irradiated–Pasteurized Fishery Products, Final Report, R. J. Learson, M. S. Schwartz, and L. J. Ronsivalli, USAEC Report TID-25544, National Marine Fisheries Service, Gloucester, Mass., 1970.

Supplementary Keywords: *food preservation; industry, food; seafood.*

Research on the radiopasteurization of seafoods carried out at the Gloucester Fishery Products Technology Laboratory has recently been reported. The report provides a summation of research conducted from 1960 to 1968, during which period the feasibility of treating haddock, pollock, ocean perch, cod and mackerel fillets, clams, lobster, blue crab, and scallops was determined. The radiopasteurization process appeared particularly promising for haddock and cod fillets. The preservation effect of radiation was apparently due to the fact that irradiation reduces the

population of microorganisms by 2 or 3 log cycles. This results in a shelf-life extension of 1 to 3 weeks at normal refrigeration temperatures.

As part of a nationwide effort to establish the safety of radiopasteurized fish, the maximum shelf life of both irradiated and nonirradiated samples was determined. The objective was to show whether irradiated samples spoil and are rejected on the basis of odor alone before botulinum toxin can develop, even in intentionally inoculated samples. These maximum shelf-life studies, or X-value determinations, were carried out on haddock and cod fillets and the three common species of Gulf shrimp.

An expert panel was created and trained at the Gloucester laboratory for odor evaluations of frozen and thawed shrimp; the panel could determine the storage age of the thawed samples to within ±1.5 days (2σ). Results indicated that there were no major differences in spoilage odor at 33°F between brown and white shrimp. The panel format was taught to researchers from Michigan State University (MSU) and the Fishery Products Technology Laboratory at Pascagoula, Miss., for use in X-value determinations with haddock fillets. Samples were then tested simultaneously at MSU and Gloucester. The X-value results indicate that temperature has a far greater effect on shelf life than does irradiation dose. At 33°F and a dose of 200 krads, samples were not rejected by a consumer panel until 20 days after the nonirradiated samples were rejected. However, at 60°F, the 200-krad samples lasted only 6 days longer than the nonirradiated samples. At any temperature, about a 100% increase in shelf life is provided by a dose of 200 krads and a 65% increase by a dose of 100 krads.

In general, geographic location seems to have little effect on judgment. In eight experiments covering four seasons, six storage temperatures, and three radiation doses, the average deviation from the Gloucester consumer panel was only 3.7 days, with no trend toward positive or negative.

Probit analysis was used to evaluate X-value data and led to these conclusions: (1) The odor evaluation panel appears to be satisfactory for X-value determinations. (2) No geographical differences among panels were evident. (3) Nomograms can be developed to predict X-values. (4) About 10 to 15% of the population risks illness through faulty judgment of food whether irradiated or not. (5) Probit analysis of X-value data and corresponding data on botulism toxin development could enable a critical determination of the safety of radiation-pasteurized fishery products.

(FEM)

Fertilizer Management Practices for Maize: Results of Experiments with Isotopes, Technical Report No. 121, International Atomic Energy Agency, Vienna, 1970 (STI/DOC/10/121).

In a joint FAO/IAEA project, in which scientists of eight countries participated, coordinated field experiments were conducted with maize during the period 1964–1968 using isotopically labeled N and P fertilizers. The same experimental treatments and techniques were used each year in order to be able to evaluate the significance not only of the treatments but also of the effect of widely differing soil and climatic conditions on their effectiveness. The primary objective of the 4-year experiment was to assess the applicability of selected fertilization practices for maize grown in different areas of the world and to provide quantitative information on the level of efficiency of use of nitrogen fertilizer by maize grown in typical maize-growing areas in selected developing countries. The data obtained clearly demonstrated the contrasting results that can be expected, depending on the environmental and soil conditions existing at an individual plot site. General guidelines conducive to sound fertilizer practices for maize fertilization were stated, based on the results of the studies. The data from individual countries are compiled into 24 tables in the Appendix. (24 references.) (MG)

Instrument Manual for Prototype Wet Concrete Analyzer by P. F. Berry and J. D. Hall, USAEC Report ORO-3842-3, Nuclear-Chicago Corp., Texas Nuclear Division, Austin, Tex. (Sept. 30, 1970).

A prototype portable nuclear gage for measuring the cement content of plastic concrete [*Isotopes and Radiation Technology*, 8(2): 146-151 (Winter 1970–1971)] has been constructed by Texas Nuclear. The instrument contains both a low-energy (^{241}Am) and a high-energy (^{137}Cs) gamma-radiation source, whose backscattered radiation is a function of the cement content of the sample. The "instrument manual" describes the analyzer and its operation in detail, giving specifications for the individual parts and units, and discusses safety features. (MG)

S. C. Bushong, J. L. Cox, V. P. Collins, J. B. Neibel, and G. B. Murphy (Eds.), *Medical Radiation Information for Litigation*, Proceedings of a conference held Nov. 21–22, 1968, at Baylor University College of Medicine, Houston, Tex. U. S. Department of Health, Education, and Welfare, Public Health Service, Report

DMRE 69-3 (Consumer Protection and Environmental Health Service, Environmental Control Administration, Bureau of Radiological Health, Rockville, Md. 20852).

Eighty-nine persons participated in a conference on Nov. 21–22, 1968, sponsored by the Baylor University College of Medicine and the University of Houston Bates College of Law, to explore the feasibility of collecting and maintaining records of medical radiation exposure for purposes of potential litigation. Papers presented related to medical and scientific factors involved in radiation dosages, disease responses, monitoring instrumentation and records keeping, litigation aspects of tort and workmen's compensation liability, causal and proof problems, factors pertinent to litigants, and the application of current legal doctrines to the problem.

Particularly highlighted were the intrinsically different objectives of radiation records keeping by the medical–scientific and the legal professions. The scientists and doctors do not agree on the magnitude of the hazard arising from radiation exposure, especially latent effects. The lawyers felt that the causal relation between radiation and disease had not been sufficiently documented to constitute legal proof as now defined. Answers to this problem were suggested in alternative proposals for reform such as lower requirements to satisfy legal proof, more comprehensive insurance programs, or substantial revisions of the law relating to liability. (MG)

M. J. Martin and P. H. Blichert-Toft, Radioactive Atoms: Auger-Electron, α-, β-, γ-, and X Ray Data, *Nuclear Data Tables, A*, 8: 1-198 (1970); available from Academic Press Inc., 111 Fifth Street, New York, N. Y. 10003.

This important compilation of decay data for 105 radioisotopes of special importance in nuclear medicine, health physics, and industry was published recently. The tables list currently accepted best values for half-lives, energies, intensities, absorbed-dose constants, and 90% absorbed-dose ranges in water. The compilation was prepared as an update of the Slack and Way publication, "Radiation from Radioactive Atoms in Frequent Use." The 105 radioisotopes listed are 69 parent and 36 daughter radioisotopes especially important in medicine. Fifty decay to stable products, and 19 decay to nuclei with one or more radioactive descendants. The article includes a review of basic radiation processes. It should be valuable to all users of radioisotopes. (FEM)

Reference Methods for Marine Radioactivity Studies, Technical Reports Series No. 118, International Atomic Energy Agency, Vienna, 1970, $3.50.

Supplementary Keywords: *chemistry, analytical; ecology; hydrology; sedimentology; biology; geophysics; oceanology; activation, neutron; material tracing; bibliography; textbook; pollution; sea; review, technical; cerium; cesium; cobalt; strontium; zinc.*

Because of the use of different experimental methods, the results of measurements of radioactivity (chiefly, natural and fallout) in marine organisms and their environment are not always comparable. In November 1968 an IAEA panel on Reference Methods for Marine Radioactivity Studies met to consider presenting, for reference, sets of analytical methods for determining selected radionuclides and corresponding stable elements. This report gives the results of the panel's studies on strontium, cesium, cerium, cobalt, and zinc.

After a brief introduction (Sec. I), the report presents sets of methods on sample collection (Sec. II), storage (Sec. III), and preparation for analysis (Sec. IV). The sample types considered for each of these operations are water, biota, suspended matter, and sediments. A general background to analytical schemes (Sec. V) then follows for both radionuclides and stable elements. Analytical methods for individual radionuclides and elements (Sec. VI) are reviewed. Eight specific recommendations of the panel conclude the report. Ten review papers that support the report are appended.

Certain of the recommendations are of particular interest in isotopes technology. They point out the need to provide marine radioactivity reference standards for intercalibration purposes, the special problem of the application of activation analysis in the presence of high concentrations of interfering radionuclides of the same element, and the necessity for a future panel to consider the additional radionuclides that are important in marine radioactive contamination (^{51}Cr, ^{54}Mn, ^{55}Fe, ^{63}Ni, ^{95}Nb, ^{95}Zr, ^{103,106}Ru, ^{110m}Ag, ^{124,125}Sb, and ^{131}I—and their stable nuclides). Perhaps of greatest interest is the recognition by the panel that "... The transport, distribution and behavior of artificial radionuclides in the marine environment are closely related to the behavior of their stable counterparts...." and that "... studies associated with labeled environments can contribute widely to the research field of biogeochemistry." This recognition leads to the recommendation that a symposium be held on the behavior, physicochemical states, and interaction of trace elements and their radionuclides. (HPR)

Analytical Control of Radiopharmaceuticals, Proceedings of a panel, Vienna, 1969, International Atomic Energy Agency, Vienna, 1970 (STI/PUB/253), $3.00.

Supplementary Keywords: *chemistry, analytical; industry, pharmaceutical; medicine; preparation, labeled material; activation analysis; chromatography; electrolysis; radiometric titration; bibliography.*

The quality of any chemical administered to patients as a drug must be controlled rigorously and stringently. Since most radioisotopes and labeled compounds now produced around the world are for medical use, both the IAEA and the World Health Organization wish to make available the information needed to ensure their proper control. To this end, the IAEA convened a panel of experts on the Analytical Control of Radiopharmaceuticals. Participants (25 from 14 countries) represented producers and users of radiopharmaceuticals and a variety of professions.

Radiopharmaceuticals are defined as compounds (radionuclides or labeled compounds) intended to be administered to humans for diagnosis or therapy. The panel papers included discussions of the organization and operation of a radiopharmaceutical control laboratory; quality control of starting materials and finished products; storage and self-decomposition of radiopharmaceuticals; specific test equipment and methods (e.g., activation analysis, chromatography, electrophoresis, autoradiography, spectrometry, and bioassay); and artifacts encountered in determining purity. The preparation of manuals of test methods and of monographs for inclusion in pharmacopoeia is described. The problems encountered by small producers are pointed out, and the responsibilities of the hospital radiopharmacy are defined. Possible roles of international organizations in the field of radiopharmaceuticals are suggested.

The publication concludes with the panel's specific recommendations on the role of international organizations and on the quality-control responsibilities of producing centers. It underlines the importance of the radiopharmacist and suggests certain information and data—of interest to both producer and user—that should be stated on the label of a radiopharmaceutical.

The book should create awareness of the need for the utmost care in quality control of radiopharmaceuticals and also should facilitate the inclusion of the required specifications and regulations in pharmacopoeia throughout the world. (HPR)

Specifications and Standards for Radiopharmaceuticals (in Spanish), Joint Publication of Junta de Energía Nuclear, Madrid, and Comisíon Nacional de Energía Atómica, Buenos Aires, Madrid, 1970.

The Spanish and Argentinian Atomic Energy Commissions collaborated in preparing this brochure; it is arranged by isotope, with each section subdivided according to compound. A typical entry, for ^{59}Fe citrate, for example, states the form of the product (isotonic, sterile, apyrogenic aqueous solution, *p*H 6 to 8), concentration, specific activity, chemical and radiochemical purities, etc., and conditions under which the product may or may not be used. Products now manufactured and planned for the future in both countries are included. (MG)

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